Archaeological and geochemical investigation of flint sources in Britain and Ireland

By

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ABSTRACT

This study investigates the archaeological use of flint in Britain and Ireland from the Mesolithic to the Bronze Age through geochemical analysis of flint samples obtained from the major areas of chalk geology within these islands (Northern, Southern, Transitional, and Northern Ireland), and provenancing of artefactual assemblages. Recent approaches to provenancing flint have demonstrated that this is indeed possible, however this approach encompasses a larger study area and provides a comparison of two methodologies, one destructive (acid digestion ICP-MS) and one non-destructive (pXRF). Acid digestion ICP-MS and pXRF are capable of detecting a range of elements in a given sample, although they each have specific advantages and disadvantages when applied to archaeological material.

There are three main research questions that are addressed in this thesis:

- Determine geochemical composition of flint samples from primary chalk outcrops;
- Assess differences between flint from different chalk provinces;
- Compare acid digestion ICP-MS and pXRF in achieving these objectives.

The results indicate that flint from the major areas of chalk geology in Britain and Ireland can be distinguished using the methodologies stated above. There are some difficulties in distinguishing between the Southern and Northern Ireland chalk province flint samples, however the samples from the Northern chalk province are very well differentiated. Archaeological assemblages chosen from throughout the study area and from a wide chronological span were sampled using pXRF and subjected to statistical analysis. This thesis represents the first study of flint from both Britain and Ireland using two different analytical methods, with results applied to a variety of archaeological assemblages. More broadly, it

provides a foundation for future geochemical analysis of flint to supplement ongoing research in this area.

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1.0 INTRODUCTION

This study outlines the archaeological use of flint during the Mesolithic to Bronze Age in Britain and Ireland, and investigates the geochemical variability of flint samples obtained from major areas of chalk geology using portable X-Ray fluorescence (pXRF) and acid digestion inductively coupled plasma-mass spectrometry (ICP-MS); in Britain, the Northern, Southern, Transitional chalk provinces and in Ireland the Northern Ireland chalk formation. This chapter outlines the nature of this research.

1.1 Flint in prehistory

Flint is a siliceous mineral found in primary deposits in Cretaceous chalk, which outcrops in the north of Ireland and in the northeast and south of England. Primary sources were exploited for raw material throughout prehistory, particularly evident during the Neolithic period when deep shafts were sunk into chalk to extract high-quality flint. These primary sources are subject to erosion from weathering and glaciation, the softer chalk is destroyed leaving behind nodules of flint, which form the basis of river gravels and glacial deposits throughout Britain and Ireland. These formed an important secondary source of flint for prehistoric people living in areas where flint does not outcrop naturally.

Flint is a very hard mineral and is extremely durable, persisting in the archaeological record over millennia. Flint tools, and the waste products from their manufacture, form the majority of evidence for many prehistoric sites throughout Britain and Ireland. Scatters of flint tools and the associated debitage have provided archaeologists with a means of interpreting past behaviour through the analysis of their creation, the *chaîne opératoire,* a concept that investigates the spatial and procedural dynamics of lithic tools (Bar-Yosef & van Peer 2009,

104), and through inferences gained into social structure and hierarchy in the case of 'prestige' objects.

Characterisation of flint has been attempted in the past using both macroscopic and microscopic analyses. Microscopic analyses were first employed in the 1970s in a small-scale study of flint from mines in the south of England (Sieveking *et. al.* 1972), to more recent broad-scale investigations (Rockman 2003; Pettitt *et. al.* 2012), with sporadic attempts being made throughout the intervening decades. Macroscopic characteristics such as colour, texture, or cortical appearance have been used as indicators of provenance, leading to references in archaeological literature to assignation of source based on colour (Conneller 2012, 98) or the presumed reliance of prehistoric people on what archaeologists today consider more appealing raw material on the basis of quality or accessibility (Briggs 1986, 188). These approaches are problematic as flint from vast geographic areas can appear the same after visual inspection, or alternatively flint from the same area can exhibit a range of colours and textures.

It is important to consider the non-functional reasons behind raw material procurement; use of certain sources, particularly flint mines, has been interpreted as due to the superior quality of flint available (Edmonds 2005, 63). However choice of raw material is not dictated only by occurrence or quality, materials may have to be both "physically and culturally appropriate" (Jones 2004, 87), involving obtaining material from distant or 'special' places, even when a suitable local alternative is available. Accurate provenancing of flint using geochemical analysis has provided an insight into the movement of raw material throughout (and between) Britain and Ireland, potentially revealing hitherto unknown connections between sources and sites.

1.2 Geochemical analysis

Geochemical analysis has been applied to a wide range of archaeological materials, e.g. obsidian, jade, turquoise, copper, silver, gold, and ceramics (Sutton 2016, 147), using a battery of analytical methods: neutron activation analysis (NAA) (Pollard *et. al.* 2007, 132), X-Ray fluorescence (XRF) (Allaby 2008, 628), acid digestion ICP-MS (Bellot-Gurlet *et. al.* 2005), petrography (Durst 2009), laser ablation ICP-MS (LA-ICP-MS) and instrumental thermal neutron activation analysis (INAA) (Gratuze 1999, 869). Geochemical analysis to detect the source of raw material relies on the 'provenance postulate', which states that in order to provenance raw material, the chemical variation between sources must be greater than the variation within a source (Weigand *et. al.* 1977).

The methodologies employed in this study are pXRF and acid digestion ICP-MS. Acid digestion ICP-MS has been described as the 'gold standard' of chemical analysis (Vanhaecke & Degryse 2012, xv) due to its exceptional sensitivity to a large range of elements at very low concentrations. Acid digestion ICP-MS analysis necessitates the destruction of a small part of the sample, a significant drawback for application to artefactual analysis. Portable XRF is capable of detecting a broad range of elements at low concentrations, and crucially is wholly non-destructive. As well as investigating the provenancing of flint, this study will provide a comparison between these methods and their suitability for archaeological research.

1.3 Study area and chronological span

For this study it was determined that a multiperiod (Mesolithic to Bronze Age) approach in terms of flint tool provenancing would provide an indication of how the use of flint varied within and between these periods of British and Irish prehistory. The Mesolithic, Neolithic, and

Bronze Age periods in these islands are often largely (if not solely) represented by scatters of flint tools and associated debitage, so increasing our understanding of the procurement and use of flint will provide greater insight into these periods of our past.

The study area encompasses the entirety of Britain and Ireland, however the focus is on the areas of flint-producing chalk geology: the Northern, Southern, and Transitional chalk provinces in England, and the chalk formations in the north of Ireland. The Southern province encompasses the south of England from Devon to Kent, extending as far north as the Thames estuary. From the Thames estuary to the Wash is the Transitional province, encompassing East Anglia and the Chilterns, including the flint mines at Grime's Graves. North of the Wash, extending along the coast to Flamborough, East Yorkshire, is the Northern chalk province. This study area omits large parts of Britain and Ireland where flint does not occur in *in situ* chalk deposits; the south of Ireland, Wales, as well as northwestern England and Scotland. Samples were obtained from each of these areas and analysed using both ICP-MS and pXRF to investigate the geochemical variability of the flint both within and between these provinces.

1.4 Analysis

Samples were collected from throughout the different chalk provinces and analysed with pXRF and ICP-MS. The results formed a 'base' dataset, which was then subject to discriminant function analysis to determine the intra- and inter-province variability in levels of twenty elements.

An artefact provenancing pilot study was conducted using five artefact assemblages, drawn from throughout the study area and representing the different periods of prehistory under investigation here. The first assemblage was collected from the Bann Valley, Northern Ireland, and is predominantly Mesolithic in date. The second was collected during a fieldwalking survey

in Kintyre, and has a small number of Neolithic artefacts, but contains mostly Mesolithic or Bronze Age tool types. The Threefords (Northumberland) artefact assemblage is early Neolithic, as is the Nether Exe (Devon) assemblage. The N1F assemblage, also from Devon, are Neolithic and later in date.

This study represents the first such analysis of both geological flint samples from throughout Britain and Ireland, and is the first to geochemically analyse such geographically diverse, multiperiod assemblages.

1.5 Research questions

There are three main research questions that form a framework for this study:

1. To determine the chemical composition of flint from primary outcrops, sampled from a number of areas with flint-producing Cretaceous chalk around Britain and Ireland. In Britain, these areas are the Northern, Southern, Transitional, and the Southwestern Chalk Provinces. In Ireland, the Northern Ireland Province contains the majority of flint-bearing chalk;
2. to assess the differences in chemical composition of flint between and within these source areas;
3. to provide a comparison between pXRF and ICP-MS in achieving these objectives.

1.6 Structure of thesis

There are a total of ten chapters within this thesis. The nine that follow the introduction are as follows:

Chapter two describes the use of flint throughout the Mesolithic, Neolithic, and Bronze Age within Britain and Ireland. It traces how prehistoric people obtained raw material, and how

procurement strategies varied in different areas. Chapter two also compares how procurement and tool typologies differed between Britain and Ireland within the same period, and suggests reasons for this.

Chapter three outlines the formation of chalk and diagenesis of flint, as well as the geological occurrence of flint within the study area. A history of provenancing studies in archaeological research is also contained in chapter three, detailing the approaches taken to analyse both native and exotic lithologies found in Britain and Ireland.

The justification for the methodologies employed during this study, pXRF and acid digestion ICP-MS, are explained in chapter four, along with discussion of the advantages and disadvantages of each approach in relation to geochemical provenancing of flint. Chapter 5 illustrates the methodology used for both pXRF and ICP-MS.

Chapters six and seven provide the pXRF and ICP-MS results, respectively. Chapter eight uses these results to provenance assemblages of archaeological artefacts. Chapter nine discusses and summaries the results in relation to broader aspects of archaeology and geochemistry. Chapter ten provides a conclusion to the thesis, identifying avenues for future research.

2. TRADE AND EXCHANGE IN BRITISH AND IRISH PREHISTORY

This chapter will explore the evaluation and conceptualisation of trade and exchange in British and Irish prehistory. The time span covered by this thesis incorporates the beginning of the Mesolithic (c. 9,600 BC (Conneller *et. al.* 2012, 1006)) and stretches to the end of the Bronze Age (700 BC (Parker-Pearson 2007, 77)). This chapter will explore the exchange and trade of flint during prehistory in Britain and Ireland. These millennia saw the introduction of agriculture and metalworking to Britain and Ireland; with concomitant social and cultural changes. The use of flint as a material for tool-making persisted throughout these technological and social changes however the means through which raw material was procured and transported went through radical changes. During the Neolithic the emergence of other lithologies had an impact on the exploitation of flint resources and the ways in which it was used for toolmaking, as did the advent of metalworking in the Bronze Age. The Iron Age period in Britain and Ireland will not be included as the widespread introduction of iron saw a significant reduction in the utilisation of lithic resources (Ballin 2002, 25).

The aim of this chapter is to review the current state of knowledge regarding the nature of trade and exchange in British and Irish prehistory, with reference to:

- How trade and exchange has been considered in archaeological discourse
- How trade and exchange can be detected in the archaeological record
- How trade and exchange can provide insights into the nature of procurement of raw material

The nature of trade and exchange during prehistory did not remain static, and there are numerous factors which influenced the procurement and movement of raw material. In reviewing historical and current understanding of trade and exchange, this chapter will provide

a background to the research questions by providing an overview of the current state of knowledge regarding procurement, trade, and exchange of raw material during British and Irish prehistory.

2.1 History of archaeological interpretation

Archaeology is the study of the human past through the recovery, analysis, and interpretation of material remains. The archaeological record is almost infinitely variable and can appear disparate and fractured; because of this, and in addition to the sheer chronological depth of the human past, archaeologists sought ways of interpreting and understanding what they encountered. To do so, conceptual frameworks and approaches that existed in other disciplines were borrowed and adapted to create coherent archaeological narratives. However, inadequacies with each conceptual paradigm that was used to interpret archaeological data led to the adoption of new modes of thought that shifted focus onto (and away from) certain issues within archaeology and changed the significance afforded to particular kinds of data (Trigger 1989, 6).

It is beyond the scope of this thesis to provide a comprehensive discussion of the evolution of archaeological thought; however this section will provide an overview of the predominant theoretical frameworks that have been adopted, adapted, and abandoned by archaeologists over the course of the last century, with reference to how trade, exchange, and procurement have been considered. These frameworks fit within culture-historical, processual, and post-processual archaeological paradigms (Gosden & Harris 1995, 419). It is important to note that these are not clearly delineated, strictly-defined methodologies in the sense that archaeologists will self-identify as a 'processualist' or 'culture-historian', or that each successive paradigm will reject wholesale the approaches of its predecessor. Archaeology as a

discipline is characterised by competing theoretical approaches, arising from different bodies of data or in response to particular issues or problems, and integrates them with others (Yoffee & Sherratt 1993, 1).

2.1.1 Culture-history

From the beginning of the twentieth century until the 1960s/1970s, the predominant theoretical framework amongst Anglo-American archaeologists used to interpret that past was that of 'culture-history'. Faced with the accumulation of abundant, diverse collections of archaeological material, archaeologists sought order; groups of artefacts with some shared feature or comparable measure were grouped together to form cultural units which were considered analogous to ethnological cultures (Webster 2008, 12; Trigger 1978, 100). This method was essentially inductive; information was obtained, organised, and explained in terms of the patterns observed. New information or observations were placed into an existing scheme, or a new one was created (Praetzellis 2015, 15).

Archaeological cultures were defined by Childe as the constant recurrence of particular kinds of material culture (Childe 1929, v-vi), which represented groups of people. The classification of archaeological material, and indeed archaeological periods such as the Thomsen 'Three Age' scheme of stone/bronze/iron (Jones 2008, 4), reflected wider societal interest in technological progress and social evolution (Vander Linden & Roberts 2011, 24), as well as contemporary historical, ethnic, and national identities (Roberts & Vander Linden 2011, 3).

This approach led to the peopling of prehistoric Europe with discrete cultural groups through the identification of stylistic similarities in houses, tools, or economy (e.g. the *Linearbandkeramik* (Hofmann & Bickle 2011, 185)). Within a culture-historical framework, changes to material culture were explained as the result of outside influence, either through

the movement from one culture to another of ideas (diffusion), people (migration), or objects (trade) (Lyman *et. al.* 1997, 212). There were, however, serious problems with this approach. Firstly, the archaeological cultures identified did not always appear to cooperate in terms of defined stylistic boundaries; as samples increased and more evidence was gathered, the blurring, mixing, overlapping, and drifting of certain types of artefact increased (Webster 2008, 16). Secondly, there was a growing realisation that the cultural identity of a particular group need not be represented solely (or at all) through artefactual remains (Bentley & Maschner 2008, 4) – it may be the case for some artefacts created by some groups, however the expression of cultural identity can be manifested through a multitude of materials or methods which may be invisible to the archaeological record (e.g. body modification, clothing). Culture-history did not develop a clear explanation for either change or stability; changes to material culture were explained through diffusion of ideas but did not provide explanations for *why* change occurred. Culture-historians, while comfortable with inter-societal adoption or copying of ideas, were reluctant to acknowledge that intra-societal innovation could occur. Another prominent criticism of culture-history was the focus on Neolithic and later societies; the pre-agricultural inhabitants of Europe were (in)famously described by Childe as helpless barbarians (1925, 1) and by Wheeler as squalid food-gatherers (1954, 231). For culture-historians, the introduction and spread of agriculture with the attendant intensification of exploitation, centralisation of power, and hierarchisation (Pluciennik & Zvelebil 2008, 467) represented the beginnings of European formalised settlement and urbanism. The proliferation of the 'Neolithic package' was viewed as being the result of demic or cultural diffusion. In this scenario, demic diffusion describes the movement and dispersal of Neolithic populations who brought with them the knowledge of agriculture and domestication of animals, whereas cultural diffusion describes the process through which aspects of the Neolithic were imitated

by indigenous groups of Mesolithic hunter-gatherers (Pinhasi *et. al.* 2005, 2220). The spread of farming in Europe was likely to be a combination of these, where trade and exchange of ideas, material remains, and movement of people were crucial.

The naivety of the culture-historical approach and the clear issues with the assignation of cultural groups on the basis of stylistic similarities led to growing unease with the inductive approach to the past, and the adoption of a deductive approach (or scientific method) grew in popularity. The deductive approach begins with a theory or hypothesis about the past against which the observed data will support or refute it (Praetzellis 2015, 16). This approach sought to understand the cultural processes behind changes observed in the archaeological record through quantification and prediction with the use of a rigorous scientific method (Gamble 2015, 31). As this method was focused on the processes behind cultural change, it became known as *processual* archaeology.

2.1.2 Processual archaeology

Beginning in the mid-20th century, processual archaeology (or *New Archaeology* in North America) was concerned with 'why', as opposed to culture-history's attention to 'who', 'when', and 'where'. Instead of describing the past, archaeologists should attempt to explain the past, identifying and explaining how and why cultures change over time through recognition of general cultural processes that dictate the development of groups through time. The reasons behind change were recognised as being important to understanding how societies function and adapt over time; these changes were interrogated using scientific methodologies focused on three areas of human behaviour – environmental, social, and ideological (Binford 1962, quoted in Gamble 2015, 31). These scientific methodologies would approach archaeology using the philosophy of logical positivism; this approach advocated a hypothetico-deductive

approach to test and define laws of human behaviour, with an emphasis on empirical data (Shafer 2009, 12). The instigator of this movement was Lewis Binford, whose 1962 paper "Archaeology as anthropology" made clear that hitherto intangible aspects of past societies could be inferred from the study of material culture. The impact of this was to empower archaeologists to move beyond classifying and cataloguing material culture, and to acknowledge the role objects play in explaining social and cultural changes or events.

The aim of processualism was to bring archaeology closer to the natural sciences, through underpinning analyses with explicitly scientific methods; subsequently processual archaeology sought to identify and explain universal cultural processes, material culture featured as a reflection of social behaviour which could be scientifically described and explained (Smith 2004, 37). This cultural materialism stresses that technology is the means through which people interact with their environment, and that technology is the determinant factor in cultural evolution (Gibbon 1984, 7-8).

Where culture-history explained consistency or change in relation to normative intra- and inter-cultural values, the focus of processual archaeology was the interplay between human cultures and their physical environments; with the investigation of palaeoenvironment, palaeoeconomy, and palaeoecology following strictly defined methodologies (Watson 2008, 30). Human cultures were viewed as systems with a complex and flexible range of interactions with the natural processes occurring around them, processualism sought to identify and understand the nature of these interactions through scientific investigation. To bridge the gap between archaeological evidence and the subsequent observations and conclusions, 'middle-range theory' developed to explain site formation processes (Landon 2010, 109). The most substantial contributions to the development of middle-range theory are the studies conducted by Binford with Nunamiut hunter-gatherers (1978) and work on faunal assemblages

(1981). The study of Nunamiut hunter-gatherers revealed the complex processes at play in the creation of bone assemblages, such as hunting conditions, meat processing, and time of year; whereas the 1981 publication outlines the various natural processes that influence the nature and condition of faunal assemblages, applying these inferences to the Palaeolithic archaeological record (Maschner 1996, 469). The works emphasise the dual consideration of archaeological observation and bodies of theory. Through this, the static archaeological record can be linked to dynamic cultural and noncultural systems (Bettinger *et. al.* 2015, 84).

Culture-historians saw trade as a vehicle for spreading ideas and objects amongst cultures, and processual archaeologists saw trade and exchange as one of the many interrelated systems that work within and between societies. As part of the zeal for increased scientific rigour regarding archaeological data, processualism saw the advent of large-scale provenancing studies of archaeological material using petrological, physical, and chemical analyses (Skeates 2009, 6). The results of these studies indicated the long-distance movement of raw material and completed artefacts. Of particular relevance for this thesis are the ground-breaking monographs detailing a raft of petrological and chemical investigations into the origin and spread of axes during the British and Irish Neolithic; Stone Axe Studies I & II (Clough & Cummins 1979 and 1983). These works are an example of the explicitly scientific and empirical nature of processual archaeology, incorporating a suite of interdisciplinary studies into the origin and transport of stone axes.

Processualist theory has many benefits for the modern archaeologist. Like the culture-historical studies before it, which provided the classificatory framework and descriptive foundation of many artefactual trajectories, processualism provides a much-needed objectivism to archaeology and demonstrates the value of incorporating scientific analyses to the study of human cultures in the past, from which inferences can be drawn. Processual

archaeology remains the dominant orthodoxy amongst archaeologists in North America (Shanks 2009, 133), part of its appeal may lie in its emphasis on technology, economy, environment, and demography – aspects of the past that leave clear traces in the archaeological record (Kelly & Thomas 2017, 32). Processual archaeology has left many positive traces in contemporary archaeological practice, particularly the development of archaeology as a science, the benefits that can be drawn from interdisciplinary studies, and the awareness that archaeologists must be more explicit about their research methods and aims (Shafer 2009, 14).

Criticism of processual archaeology was outlined during the 1980s and 1990s. The main proponent of this was Ian Hodder, who, inspired by postmodernism, advocated an increasingly relativistic approach to the archaeological record (Maschner 1996, 109). Processualism relied on empirical data and scientific analysis and observation to investigate archaeological material under a distinctly positivist approach, that is, that there is an objectively knowable past that can be revealed through adherence to scientific methodologies. Hodder and others instead argued that a relativist standpoint, the understanding that no universal criteria exist with which archaeologists can compare/judge customs, beliefs, values, and interpretations, was required to fully assess the material remains from past societies (Thomas 2000, 4).

Processual archaeology developed and applied necessary scientific standards to archaeology, in opposition to the subjective groupings of similar artefacts in culture-historical approaches, however processualism represents a rather one-dimensional view of archaeological data (Kristiansen 1984, 73). What was absent from processual approaches to material culture was the acknowledgement that artefacts are not purely economic items, they can be imbued with symbolism and meaning and should be considered in light of their cultural, ideological, and historical contexts (Hodder 1982, 207). Within the study of material culture, it was no longer

enough to describe raw materials or artefacts in quantitative terms, the context of an object was crucial – consideration of objects and trade that focused solely on economy captured only part of their meaning (Agbe-Davies & Bauer 2010, 20).

To facilitate conceptualisation of the full meaning of artefacts, drawing on their cultural, social, and symbolic significance to the cultures that created or encountered them, a new approach was required. Post-processual archaeology encouraged the integration and engagement with theoretical advances made in other disciplines, principally anthropology, to engender interpretations of the archaeological record that moved beyond the descriptive or the analytical (Hodder & Hutson 2003, 206).

2.1.3 Post-processual archaeology

Culture-history and processual archaeology can both be described as having overarching guiding principles that justify the description of these approaches as coherent theories. Post-processual archaeology cannot be described in these terms. 'Post-processual' defines the suite of theories, approaches, and methods used to explain the archaeological record in the decades since the 1970s/1980s arising from criticisms of processual archaeology and culture-history. The trends and perspectives included under the umbrella of 'post-processual' archaeology include structuralism, feminism, and phenomenology (Shanks 2008, 133). These various perspectives can be easier defined by what they are *against* than what they are *for,* namely the use of positivist, functionalist analyses in an objective, scientific framework (Mithen 1989, 483).

Due to the sheer variety of conceptual standpoints that fall under 'post-processualism' it is not possible to provide a comprehensive review of them all. However, they do share some common features. The post-processual paradigm(s) do not claim to predict or understand the

past; rather the various methods and viewpoints included in post-processualism are inherently critical and examine the contemporary social and cultural context in which discourse about the past is created and evaluated (Kohl 1993, 13). The predominance of context is based on the view that artefacts are enmeshed and inseparable from their cultural settings which create and maintain social relationships and can consolidate the power of privileged groups (Erikson & Murphy 2013, 125).

Hermeneutics is the study of meaning or interpretation (Gosden 1999, 470). Hermeneutics as applied to post-processual archaeology outlines the manner of reasoning that moves between "past and present…different categories of data, archaeological evidence, oral history, written sources, ethnographic data, anthropological theory, and human experience" (Yamin & Bescherer Metheny 1996, xiv). Developing, evaluating, and redeveloping theories and interpretations in this manner is known as the hermeneutic circle; post-processual archaeology engages with this wholeheartedly as a means of understanding human life in the past. In this sense it is markedly different from the empirical, positivist approach of processual studies.

The conceptualisation of theories or explanations to account for the behaviours observed in the archaeological data is not conducted in a vacuum; post-processual archaeologists acknowledge that every observer will construct the past in different ways as they will draw on their own individual life experiences, beliefs, values, and customs. In asserting that there is no objectively knowable or identifiable 'true' past, post-processual archaeologists instead opt for a relativist approach; a belief that no universal criteria exist with which we can explain the past and that interpretations of the past are subjective. This is in direct opposition to the approach of the processual archaeologists who aimed for objective truth through empiricism and scientific analyses. The relativist approach does not simply mean that 'anything goes' in terms of archaeological interpretation; a distinction is made between epistemic and judgemental

relativism where epistemic relativism maintains that knowledge is created in relation to the social and cultural context and judgemental relativism holds that all knowledge is of equal value (Whitley 1998, 33). The criticisms of judgemental relativism are obvious; a particularly damning assessment is that a state where all views of the past are of equal value leaves room for politically undesirable or prejudicially-motivated interpretations, such as Holocaust denial (Johnson 1999, 171). This example is, of course, an extreme one. In practise, contemporary archaeologists are neither wholly positivist nor relativist, there is acknowledgement that archaeologists are inextricably linked to their own social and political circumstances and that archaeological data, while important, do not exist in an unbiased way (Johnson 1999, 175).

Economy, trade, exchange, and subsistence, which were so often the focus of processual archaeologists, did not feature prominently in post-processual literature due to the shift of attention on to ideology and symbolism (Age-Davies & Bauer 2010, 13). However, these topics were reconciled and reintroduced to archaeological discourse with the recognition that the underlying meaning of, for example, exchange of an object, was more significant than the act of exchange itself (Chapman 2008, 335). The approach to trade and exchange in previous theoretical approaches focused on the quantification and classification of object types or numbers of items, as well as chemical or petrographic analysis of material, focusing on the inferences that can be drawn about the society that created or obtained them; the objects themselves were passive, not considered interesting enough in their own right to warrant detailed investigation. On the contrary, post-processual archaeologists regard artefacts as active participants in their social and cultural contexts, objects with agency, matter has innate power and is continually in flux (Thomas 2015, 1288-9).

Prior to the advent of post-processualist archaeology, there was little to no emphasis on the individual, except within processual considerations of ‘Big Men’, chiefs, and leaders – even

they were evaluated in terms of their perceived power and influence within their cultural and societal systems (Whittle 2003, 51). One of the major distinctions between processual and post-processual archaeology is the consideration of the individual. Whereas processual archaeology did not consider the individual as an active participant in their society (in fact people were viewed as being comparatively constrained by their social and cultural environment), post-processual archaeology highlighted the role of the individual and recognised that people (including, crucially, women and children) were necessary for the construction, maintenance, and negotiation of their relationships with society (Orsner Jr. 2002, 444).

The acknowledgment that the archaeological record was created by people who were acting with purpose, intent, resistance, and capacity is the central tenet of agency theory; a sociological and philosophical approach that addresses the relationships between an individual and all diverse aspects of their human experience (Gardner 2007, 1). Questions of agency have existed for millennia within philosophical discourse however such perspectives have only been applied to archaeology in within the last 30-40 years (Dornan 2002, 303). Key concepts of agency were developed by Giddens and Bourdieu, 'duality of structure' and 'habitus' respectively.

Duality of structure is a process where people are dependent upon the rules and resources of societal structure, but also where they have a conscious choice in manipulating these structures (Gardner 2007, 3). *Habitus* refers to the ways in which people defines themselves through repeated actions and behaviours crucial to social practice; habitus is learned and tells us what is acceptable and proper within societal and cultural boundaries (Greene & Moore 2010, 284). Under processual studies, technology was divorced from its social context in the

pursuit of objectivity, however to consider agency is to accept and acknowledge that people and technology have a dialogue, and become shaped by one another (Dobres 2000, 127).

In this sense it can be said that both objects and people have agency, and both actively participate in the formation and maintenance of social relationships. Leading from this, objects can be described as having their own biographies; they exist within society from manufacture to deposition and can accumulate histories over time (Joy 2009, 540). The concept of object biography or 'the cultural biography of things' was presented by Kopytoff (1986) and has had a profound effect on the way in which material culture is considered within post-processual frameworks (Fontijn 2013, 183). Kopytoff outlined the features of a culturally-informed object biography, including its culturally-constructed identity, the specific cultural relevance of the object, and the trajectory of its life from manufacture (birth) to deposition (death) (Kopytoff 1986, 68).

Post-processualism has attracted a great deal of criticism, not least from proponents of processual archaeology who considered the relativist approach, the lack of clear methodology, coupled with no clear aims and methods as traditionally outlined in quantitative investigation, an indication that post-processualism is not 'science'. The description of processualism or post-processualism as 'science' is almost a moot point as it relies on how science is conceived – there is more than one approach to scientific enquiry (Shanks 2008, 138). There is also a perception of post-processual archaeology as being rooted in a tangled corpus of difficult, irrelevant theory (Shanks 2008, 133) compared to the clarity of the processual approach with its rigid methodologies and basis in quantitative data. Post-processual approaches have also been accused of hastening the fragmentation of archaeological discourse, with the "…endless generating and forgetting of mini-paradigms…with minimal differences between them" (Mizoguchi 2015, 16).

The difficulty with evaluating the usefulness of post-processual archaeology is perhaps due to the fact that post-processualism is not a coherent theory of the past. As mentioned above, post-processualism is the term given to the raft of new approaches to archaeological material following criticisms of processual practice. It is maybe best to conceive of post-processualism as an 'era' rather than a movement or analytical framework, or to consider the co-existence of post-processual *archaeologies*. The speed with which post-processualist ideas and academic debate flourished in archaeological literature led to theory wars, intense criticism of and from processualist archaeologists, and increasing polarisation between 'processualists' and 'post-processualists' (Shanks 2008, 139).

Archaeological research in the early 21st century now finds itself in an unusual position. Increasing improvement in scientific methodologies and greater access to highly sensitive instrumentations has resulted in an explosion of studies into subjects considered forbidden under a traditionally post-processualist perspective – particularly obvious in large-scale research projects focusing on evidence for migration, raw material movement, and grand narratives of human origins (Kristiansen 2014, 13-4). With these studies however comes detailed social and cultural contextualisation of the findings; modern-day archaeological research is fully aware of the need to marry the hitherto disparate ideological and quantitative strands within the discipline to provide a more comprehensive understanding of past societies.

2.2 Trade and exchange in archaeology

Trade and exchange are perhaps among the most enduring concepts in archaeological research. The identification of traded goods was contingent upon the recognition that some aspect of an object (e.g. raw material or stylistic variation) differed from the material culture of

the location where it was found, implying therefore that it had originated elsewhere (Renfrew & Bahn 2005, 32).

The shifting paradigms of archaeological theory have taken very different approaches to trade and exchange as evidenced through material culture. Trade featured prominently within culture-historical and processual archaeologies. For culture-historians, with their emphasis on typology and classification, material remains in different cultures which shared stylistic similarities were viewed as the product of diffusion. Conversely, objects which were exotic in terms of raw material or which differed stylistically or aesthetically were explained as the influence of another culture. For culture-historians, trade was therefore the means for the spread of ideas and objects between cultures (Agbe-Davies & Bauer 2010, 30).

By the late 1960s however, diffusion could no longer explain the increased evidence for interregional interaction (Oka & Kusimba 2008, 346). Processual archaeologists viewed trade as one of many systems which operated within and between cultures. Quantification of imported objects within a material assemblage replaced ideas of diffusionism as the primary way in which archaeologists attempted to understand the past (*ibid*.). The emphasis on quantification and empiricism led to a number of studies where material remains were subject to chemical analysis. The beginning of this, and considered the seminal work, was the characterisation of obsidian sources in the Aegean by Renfrew *et. al.* (1965). This study was highly significant as it used empirical data to interrogate ideas of social complexity and reconstructed source histories and raw material distribution (Carter 2014, 23). Investigation of long-distance trade sat well within processualist methodologies as the chemical characterisation of archaeological materials could provide hard data to unequivocally demonstrate the existence of trade in the past. Within a processualist framework, trade was viewed in ecological and functional terms, and there was little attempt to move beyond data

to access the ideological or symbolic aspects of trade (Mellars 2009, 502, 516). With the beginning of post-processual consideration of archaeological material there was an increasing awareness that trade was not purely an economic exercise, and that it is the intra- and intercultural relationships that are created through the process of exchange that can provide greater depth to our understanding of past societies.

The post-processualist era saw the explicit integration of ideological, social, and historical concerns in archaeological discourse. Whether consciously or unconsciously, post-processual archaeologists tended to marginalise the studies of trade and exchange which were the focus of processualist positivist, functionalist approaches. Trade and exchange were reintegrated into archaeological research through the acknowledgment that the meanings behind exchange could take precedence over inferences of sociological behaviour (Chapman 2008, 335). From a post-processual perspective, movement of objects or raw material was not simply a quantitative exercise but an opportunity to engage with the priorities and preoccupations of prehistoric societies, whose choice of raw material and acquisition of certain exotic objects were deliberate and loaded acts. The post-processual approach to trade and material remains was established by Hodder who articulated the need to consider objects of trade in light of their cultural, ideological, and historical contexts (Hodder 1982, 207).

The approach to trade and material remains in contemporary archaeological research can be viewed as a synthesis of particular aspects of culture-history, processualism, and post-processualism. The typological and classificatory foundations used today draw heavily on the work of culture-historians, and the identification of objects that do not fit within the stylistic tradition observed in a certain area are frequently interpreted as the result of trade. The contribution of processual archaeology is that it provides a methodological and analytical framework with which to apply the suite of analytical techniques now available to a wide

variety of archaeological material. Compared to the 1960s and 1970s when processualism dominated discussion, the early twenty-first century has an embarrassment of riches in terms of the choice of analytical procedures and instrumentation that can be used to investigate material remains. The application of these methods has provided an almost unimaginable amount of data relating (but not limited) to chemical composition, petrography, isotopic variation, and aDNA, with which narratives of trade, migration, nutrition, ecology, and subsistence have been constructed. Although post-processual archaeology rejects many of the central tenets of both culture-history and processualism, they have exerted a profound influence. Post-processual archaeology still relies on the classifications and typological sequences established by culture-historians, although the inferences drawn about past societies and material remains differ significantly. Similarly, post-processual archaeologists no longer reify the scientific approach or seek objective truth; however aspects of prehistory as investigated by post-processualists (e.g. trade, migration) can be complemented through application of scientific methodologies. The character and social contexts of material remains or trade cannot be extrapolated from one kind of data (Bradley & Edmonds 1993, 16).

The wider contexts of artefacts is the priority in the post-processualist era, and in theorising, debating, and challenging the inferences made, both the classification and quantification are now seen as necessary components.

2.3 The British and Irish Mesolithic

2.3.1 Flint tool industries

The early Mesolithic period saw the return of human occupation to Britain and the beginning of a human presence in Ireland, although an earlier occupation has been evidence based on dating of butchered faunal remains (Dowd & Carden 2016). The earliest Mesolithic occupation of Britain is dated to c.9500 cal BC at Howick (Boomer *et. al.* 2007, 89); whereas Ireland is colonised a millennium later, with dates from Mount Sandel stretching back to 8340 cal BC (Kimball 2000, 2; Tolan-Smith 2008, 139). Meltwater from receding ice sheets raised sea levels, separating Britain from continental Europe around 6500 BC (Mithen 2007, 35). Retreating ice sheets also caused the isostatic rebound of northern Britain and Ireland; this outpaced the rise in sea levels leaving behind 'raised beaches' that define the Late Mesolithic coastline (Dyer 1990, 23). Isostatic rebound has undoubtedly obscured many earlier Mesolithic coastal sites, particularly in northern Europe (Price 1991, 215). In Britain and Ireland, evidence of early Mesolithic occupation is frequently inferred from identification of lithic scatters and/or midden deposits (Telford 2002, 290; Callaghan & Scarre 2009, 360).

The earliest Mesolithic assemblages found in Britain are composed of microliths, small retouched implements that were hafted to form composite tools (Andrefsky 1998, 207) (Figure 2.1). A bipartite division in British Mesolithic microliths can be made as the early Mesolithic is characterised by broad-blade microliths, with narrow-blade microliths introduced in the late Mesolithic (Tolan-Smith 2008, 140). However, the model of 'broad-blade = early Mesolithic' is challenged by flintworking traditions in Scotland and Ireland, as will be discussed below.

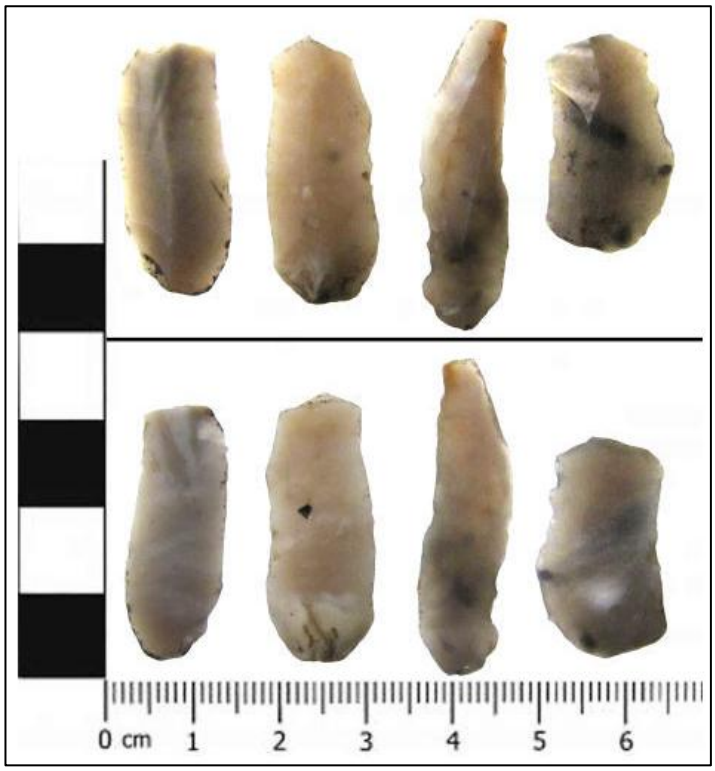


Figure 2.1 - Early Mesolithic microlithic tools, Lincolnshire (Portable Antiquities Scheme (PAS) 2013a)

During the early Mesolithic in England, microliths were formed from relatively broad blades, shaped using microburin technique (Figure 2.2), where a blade is notched and then snapped, leaving non-geometric fragments that are used to create microliths. The waste fragment is the microburin, showing characteristic traces of the notch used to snap the blade (Andrefsky 1998, 258).

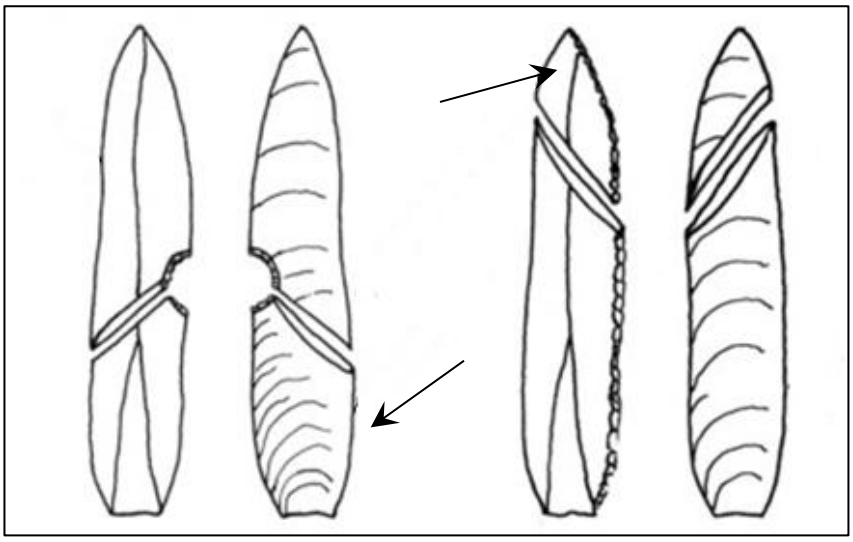


Figure 2.2 - Microburin technique on a blade (microburins arrowed) (after Henry 1974)

'Broad blade' assemblages are generally shaped like isosceles triangles or are described as obliquely-blunted points (Mithen 2007, 38). Broad blade sites are found across Britain during the early Mesolithic and are very similar to assemblages found in northern Europe; this industry is termed the Maglemosian and has been interpreted as a pan-northern European cultural phenomenon (Sørensen 2012, 256). Broad blade assemblages can be subdivided into three distinct technological types; Star Carr, Deepcar, and Horsham types.

Substantial evidence for early Mesolithic occupation begins between 9600-9000 cal BC, and flint assemblages from this period are dominated by 'Star Carr' and 'Deepcar' types (Tolan-Smith 2008, 140). 'Star Carr' type assemblages are characterised by broad obliquely-blunted points with isosceles triangles and trapezes, whereas 'Deepcar' sites are distinguished by slender obliquely-blunted points, rarely found with isosceles triangles (Figure 2.3) (Spikins 2010, 15). The 'Horsham' type assemblage appears during the early Mesolithic and differs from Star Carr and Deepcar types, as these hollow-based points are largely confined to the southeast of England (Mithen 2007, 38).

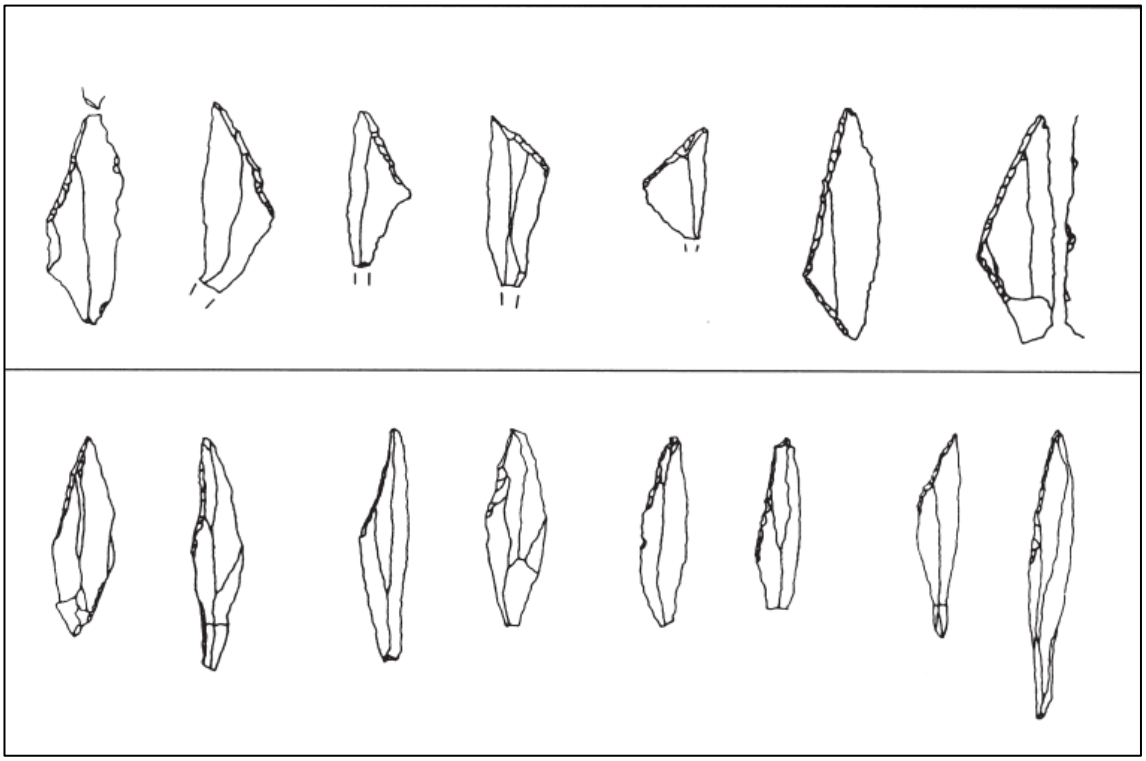


Figure 2.3 - Star Carr type microliths (top) and Deepcar type microliths (bottom) (Barton & Roberts 2004, 343).

While the early Mesolithic record in England is dominated by broad blade sites, Scotland and Ireland appear to follow different flintworking trajectories. Scottish early Mesolithic sites have produced typologically late Mesolithic narrow blade assemblages (when compared to the English early Mesolithic), without reliably dated broad blade assemblages to account for early Mesolithic occupation in Scotland (Saville 2004, 7). The early Mesolithic in Scotland is instead represented by narrow blade sites, such as Cramond, Edinburgh, from which radiocarbon dates were obtained that placed narrow blade technology in Scotland at 8600-8200 BC, prior to its typically 'late' Mesolithic occurrence in England (Reed 1995; Council for British Archaeology News 2001). The relationship between the early narrow blade technology in

Scotland and the broad blade early Mesolithic in England is, as yet, unclear; although this may be refined through further research into the populations living on the North Sea Plain and their movement into Britain (Scottish Archaeological Research Framework (ScARF) 2013).

In Ireland, the early Mesolithic is characterised by narrow blade technology (Figure 2.4), dominated by geometric microliths, scalene triangles (Figure 2.5), backed blades, core and flake axes, awls and scrapers (Driscoll 2006, 56), as well as forms unique to Ireland, such as flaked axes and needle points (Costa *et. al.* 2005, 19). This technology is shared with the Isle of Man and differs significantly from the lithic industries in Britain at this time, and is regarded by some as an insular development (e.g. Costa *et. al.* 2005, 23). The lithic assemblage recovered from Mount Sandel is among the earliest found in Ireland; if it is truly a native development it may indicate that it is not representative of the earliest occupation in Ireland (Woodman 1985, 171), particularly relevant in light of the recent dating of a butchered bear patella dating to 12,800-12,600 BP, pushing back human occupation of Ireland to the Upper Palaeolithic (Dowd & Carden 2016).

Figure 2.4 - Irish Early Mesolithic narrow blades, Antrim (after Woodman 2010, x)

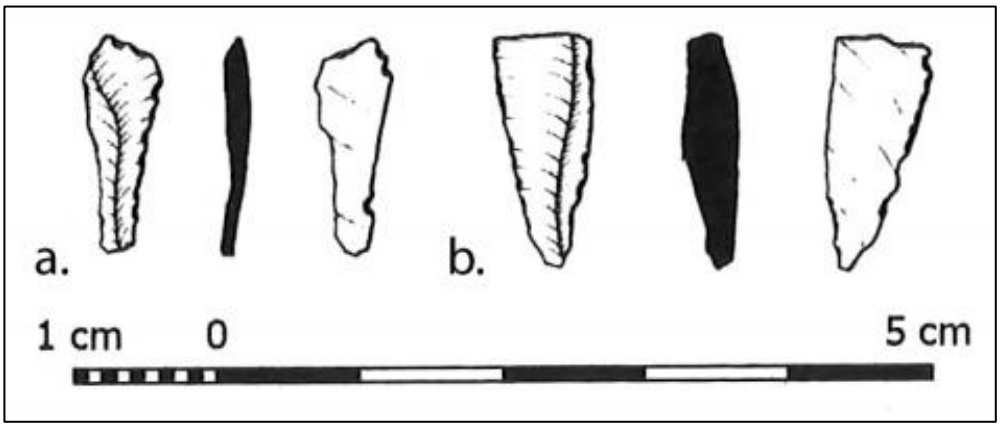


Figure 2.5 - Irish Early Mesolithic scalene triangles, Antrim (after Woodman 2010, xiv)

The tool-making industries in the early Mesolithic are generally focused around exploitation of flint resources; however there are a number of localised traditions which utilise other lithic sources.

The early Mesolithic site at Kinloch, Isle of Rhum dates to 7760-7470 cal. BC (Tolan-Smith 2008, 138). The majority of the worked stone was fashioned on the local bloodstone, which knaps in a similar manner to flint. The microlithic component of the assemblage was represented by backed blades and crescents, as well as scrapers and edge retouched pieces (Wickham-Jones *et. al.* 1984). The noteworthy aspect of the Kinloch lithic assemblage is the predominance of bloodstone, despite the availability of local flint, demonstrating the adaptability of early Mesolithic groups exploring new territories.

The late Mesolithic period is conventionally defined by the widespread appearance of new forms of lithic technology, although in some cases these tool types were already present in early Mesolithic assemblages (Tolan-Smith 2008, 147). Broadly speaking, the late Mesolithic in England and Wales is characterised by microliths made on narrow blades; however this does not apply for the Scottish late Mesolithic, where narrow blade technology was present at the earliest stages of the Mesolithic period and continued into the early Neolithic (Finlay *et. al.* 2002, 107; ScARF 2013).

The emergence of new lithic forms, and by extension the late Mesolithic, occurs at different dates throughout Britain and Ireland. Recognisably late Mesolithic sites appear in England c.7500 cal BC; these sites are generally microlith-dominated and situated in upland locations - although there is an enormous variety within and between assemblages, and the period is generally poorly understood (Spikins 2010, 17). Changes in lithic technology associated with the late Mesolithic occur somewhat later in Ireland; the site of Newferry, Antrim is considered a late Mesolithic 'type site' and dates to approximately 6500 cal BC (Costa *et. al.* 2005, 19; Kador 2010, 149)

The later Mesolithic in Ireland provides evidence for a macrolithic tradition, which is distinct from developments both in Britain - where narrow blade industries predominated - and continental Europe, where microliths were crafted on broad blades (Blankholm 2008, 112-3). However, there is a danger of simplifying the flint tool typologies and technologies in production during the late Mesolithic (Woodman 2005, 140), which may obscure inter- and intra-assemblage variations. These variations manifest as differences in raw material procurement and reduction strategies, as well as localised distribution of discrete tool types - some of which appear more frequently than others, and will be discussed below (Kador 2010, 145).

The change in lithic technology that occurs at the early/late Mesolithic juncture has not been conclusively justified, although there have been a number of hypotheses to account for the (often drastic) change in production methods, including (but not limited to): new technological/cultural traditions, shift in territorial exploitation patterns (Costa *et. al.* 2005, 20); emergence of specific stylistic identities (Cooney 1993, 634), geographical isolation of areas such as Ireland or environmental factors (Woodman 2009, xxxix). In Ireland, dated sites for the early and late Mesolithic are separated by a period of c.500 years (Woodman 1978, 2000); this may well be due to a lack of archaeological interest or simply bad luck, however the stark differences in the lithic technologies on either side of this chronological gap warrant further investigation.

The late Mesolithic in Britain and Ireland is defined through the identification of flint tool industries that exhibit different reduction techniques and new types of tools when compared to early Mesolithic assemblages. The greatest differences between early and late Mesolithic toolmaking traditions are seen in the abrupt changes in bone and antler working, which emphasise the distinction between the early and late Mesolithic periods more clearly than the

gradual changes in flint technologies (Tolan-Smith 2008, 147-8). The non-flint industries will be discussed in a later section.

The late Mesolithic flint tool repertoire had its origins in the early Mesolithic; microliths continued to be used in the south of Britain on narrow blades, however there is a trend towards increasingly geometric forms (Figure 2.6) and a reduction in size (Mithen 2007, 38). It has been suggested that Britain, particularly the south, could be interpreted as being culturally distinct from Ireland and northern Europe during the late Mesolithic, based on the persistence of narrow blade microlithic technology and apparent reluctance to integrate polished or ground stone axes into their repertoire (Kador 2010, 155).

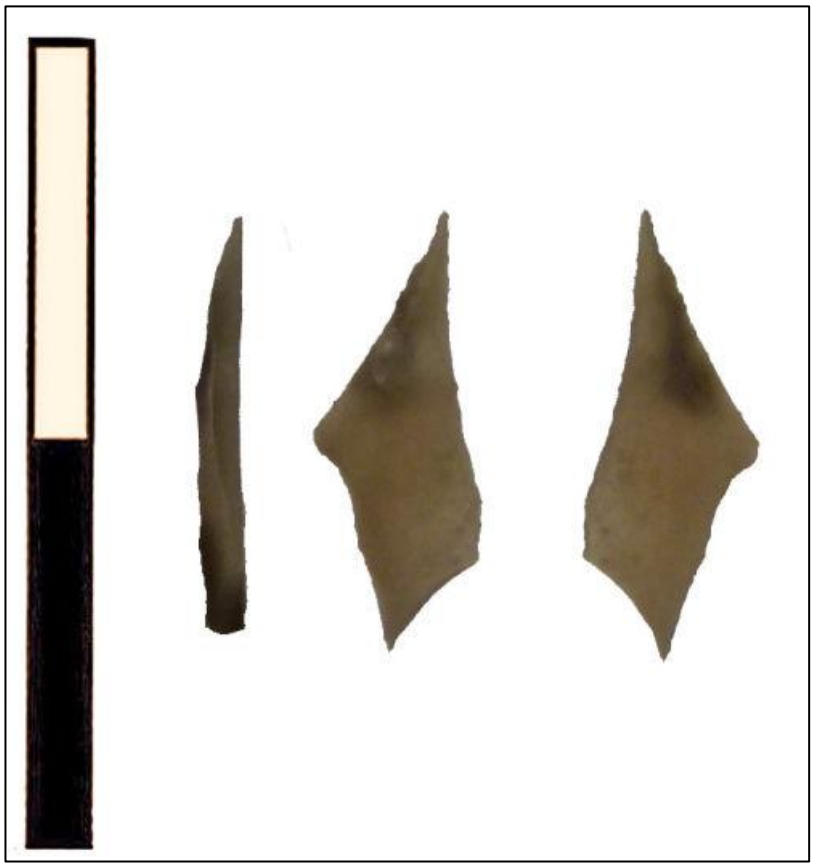


Figure 2.6 - Late Mesolithic geometric microlith, Lancashire (PAS 2013b)

Although polished and/or ground stone axes were not a feature of the late Mesolithic in southern Britain, there were a number of non-microlithic tools in production at this time. These included flaked flint axes (Figure 2.8), scrapers and awls (Hosfield *et. al.* 2007, 49).

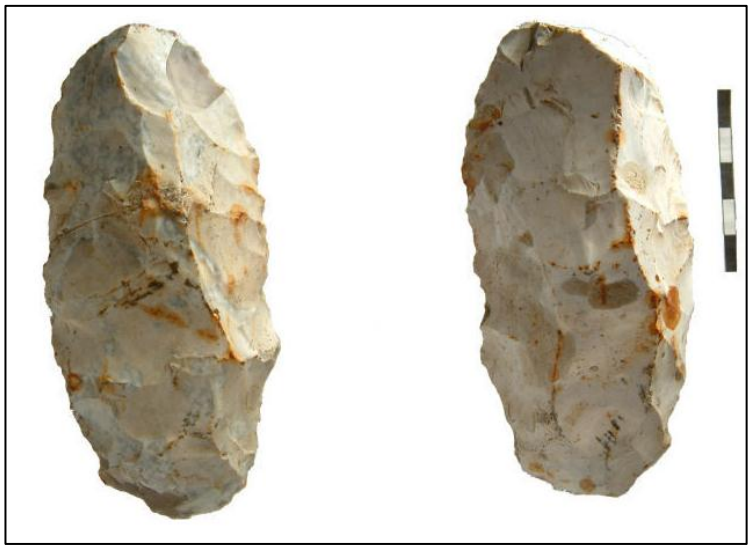


Figure 2.7 – Late Mesolithic flaked flint axe, Wiltshire (PAS 2013c)

The shift to narrow-blade microlithic technology is interpreted by Mithen as a reflection of new hunting strategies (2007, 38), however the change in lithic technology at this time is likely to be due to the cumulative effect of a number of reasons, including environmental changes and emergence of new cultural traditions (Hosfield *et. al.* 2007, 49). The separation of Britain from continental Europe at the beginning of the late Mesolithic, c.7500 cal BC (White *et. al.* 2000, 1), may provide an explanation for the change in lithic technology. It has been asserted by some that Ireland's geographical isolation is the cause of the distinct flint industries in the early and later Mesolithic (Cooney 1993, 634; Woodman & McCarthy 2003, 36); the distinct flint technology during the late Mesolithic of southern Britain may have similar origins, as similarities with early Mesolithic Maglemosian industries cease c.7500 cal BC (Myers 2006,55).

The Irish late Mesolithic is identified by the complete abandonment of the microlith-using, composite tool tradition, and the emergence of a new technology based on large broad flakes, which are retouched into a number of multi-purpose hand tools, e.g. knives and reamers (Costa *et. al.* 2005, 20). The late Mesolithic in Ireland is defined by the Bann flake (Figure 2.8), as the early Mesolithic is defined by the microlith.

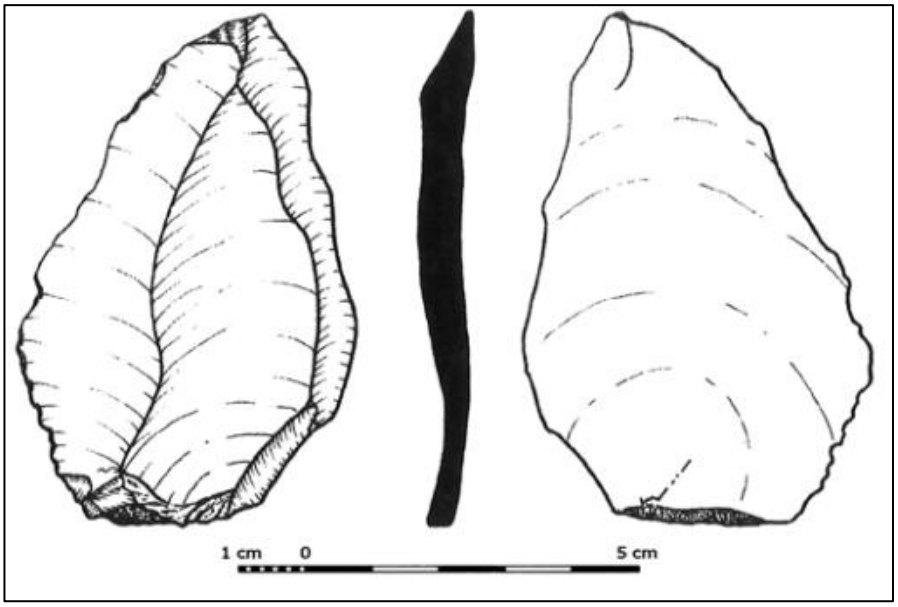


Figure 2.8 - Bann Flake from Newferry, Antrim (Woodman 2010, xvi)

Bann flakes are found only in Ireland and the Isle of Man during the late Mesolithic, although there is also a suggestion that Larnian-style (figure 2.9) flakes have been discovered on the Scilly Isles (Ashbee 1986, 195). The Larnian technique involves the creation of several large blades detached from a uniplane core using hard hammer percussion; the core is abandoned when a flat knapped surface is created (Woodman 2009, xli). On the Isle of Man they are found in association with early Neolithic archaeology, leading some to suggest that although their production and use originated in the late Mesolithic, the tradition flourished at a later date on the Isle of Man (McCartan 2003, 334). Previously considered an archaeological culture, the

Larnian ‘artefacts’ (mainly flakes and leaf-shaped points) are now viewed as waste products from flintknapping (O’Kelly 2005, 64). Bann flakes are large, butt-trimmed, leaf-shaped blades, with minimal retouch, created using a uniplane core.

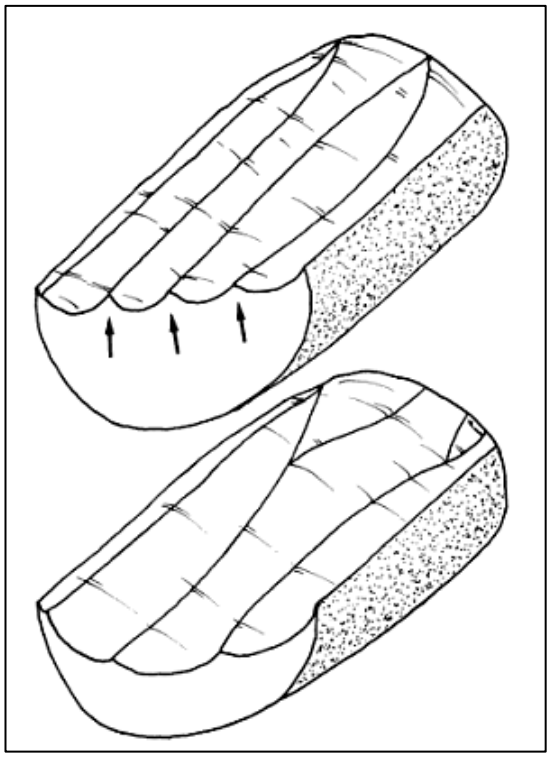


Figure 2.9 - Larnian core schematic (Woodman & Andersen 1990, 379)

The Mesolithic period has been traditionally interpreted within a processualist framework as being characterised by highly mobile bands of hunter-gatherers with low levels of social and/or economic complexity (Spikins 2008, 4). This view has been challenged with the discovery of sites with evidence for (semi) permanent structures such as Star Carr (Clark 1954); Howick (Waddington *et. al.* 2003) and Mount Sandel (Woodman 1985). However, the movement of flint many tens of kilometres across the landscape suggests that there was a degree of movement or exchange between hunter-gatherer groups living in different areas (Conneller & Schadla-Hall 2003, 88). The processual view on hunter-gatherer mobility is that of reaction to

environmental changes, where movement of hunter-gatherers was undertaken as a consequence of circumstances beyond their control (Kador 2007). The possibility of semi-sedentary early Mesolithic groups is suggested by the occurrence of (apparent) regionalism of different flint industries. The early appearance of the narrow blade industry in Scotland and Ireland is juxtaposed with the traditional 'English' model of the Mesolithic period; narrow blade industries, with the apparently distinct, non-microlithic bone- and antler-tool using 'Obanian' (a view of the Scottish Mesolithic now discarded (ScARF 2013)) in Scotland and later macrolithic developments in Ireland, indicate that flintworking at this time was not simply a means to an end, and may have resulted from lack of contact or isolation, or been a manifestation of cultural identity, as has been suggested for the Irish Mesolithic period (Woodman 2009, xxxix).

The early Mesolithic toolkit in Britain and Ireland can be loosely described as microlith-based, however as has been demonstrated, there are a number of flintworking trajectories that create an overall impression of localised adaptation. The choice of raw material in the early Mesolithic appears confusing at times; the utilisation of inferior local material at Toome Bridge is difficult to explain in the context of supposed large-scale transport of high-quality coastal flint throughout the Bann Valley (Kimball 2000, 53; Woodman 2009, xli). Likewise, preference for bloodstone on Kinloch despite availability of local flint suggests that there were non-utilitarian factors at play in the early Mesolithic in terms of choosing raw materials. In the Western Isles of Scotland, flint was imported to sites such as Ulva (Bonsall *et. al.* 1992; 1994), demonstrating the possible symbolic importance afforded to exotic or unusual material. This may also be the case in the Vale of Pickering, where coastal sources were preferentially used over the local gravel flint at some sites, despite the long distances required to obtain it (Conneller & Schadla-Hall 2003, 100).

These differences in tool-making traditions, particularly in the dissimilarity of the later Mesolithic flint tools and those found in Britain, does not equal a lack of contact between these islands during the Mesolithic. Britain and Ireland were populated for millennia with Mesolithic hunter-gatherers, and in the case of Ireland populated *by* hunter-gatherers most likely crossing the sea from Britain. To consider the differences in tool-types as evidence of a lack of contact is therefore untenable. The style of an artefact or assemblage does not constitute an index of interaction, and pointedly, differences in material culture can occur amongst proximate groups as a means of differentiation or self-expression (Thomas 2015, 977).

The difference between tool types in Ireland and Britain during the Mesolithic has been interpreted as the result of the different environment and ecological conditions that existed. Within Ireland, the largest terrestrial mammal was the wild pig, whereas deer existed in Britain and Europe. Aside from pig, subsistence in Mesolithic Ireland was likely reliant on fishing, gathering, and coastal resources such as shellfish or marine species (Woodman 2015, 237). Archaeologists have linked the relative paucity of prey animals in the Irish Mesolithic with a static, homogeneous tool industry. This view of the Mesolithic period in general – as static, unchanging, at the mercy of environmental conditions – has been rendered virtually unrecognisable through the literature emerging since the emergence of post-processual archaeology. Stasis or flux in tool types cannot be interpreted as simply the result of environmental stress.

2.3.2 Exploitation of primary and secondary deposits of flint in the British and Irish Mesolithic

The post-glacial colonisation of Britain and Ireland relied upon the availability of the requisite resources to sustain a Mesolithic way of life. Aside from sustenance, flint was arguably one of

the most important resources, from which the principal components of the Mesolithic toolkit could be manufactured. Primary sources of flint in Britain and Ireland are found in bands or nodules within Cretaceous chalk deposits, or occasionally as ‘clay-with-flints’ outcrops on chalk downs (Figure 2.10) (Butler 2005, 18).

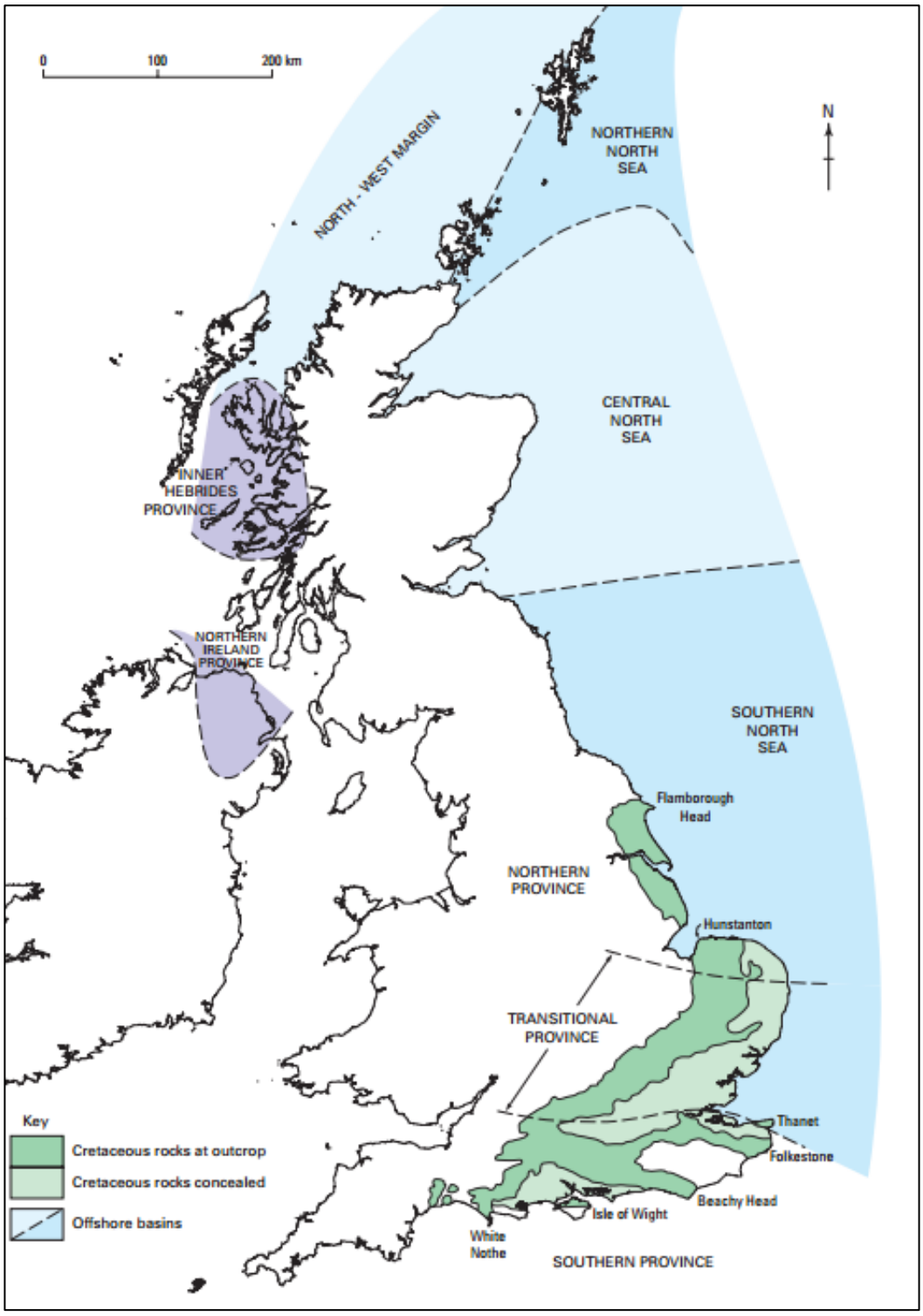


Figure 2.10 - Upper Cretaceous Provinces in Britain and Ireland (after Hopson 2005, 2)

As well as these primary, *in situ* deposits, secondary sources of flint in the form of beach and/or gravel pebbles can be found in glacial drift deposits across the majority of Britain, the origin of this flint may be from offshore outcrops (Saville 2011, 7). The flint found in primary deposits is preferable for knapping, as it does not contain the internal flaws and fissures that are common in mechanically weathered pebbles (Butler 2005, 19). However, the view that secondary sources of flint are generally inferior is not necessarily accurate. Flint pebbles that have been moved through glacial action can be knapped economically and produce durable tools, as the flawed nodules get broken down quickly, while the strongest nodules survive (Briggs 1986, 188). In Ireland, the primary and secondary sources of flint are generally restricted to the northeast of the country (Driscoll & Warren 2007, 5); sources of flint are almost entirely absent from the midlands of Ireland (Briggs 2001, 42). Secondary deposits are especially significant in the north of Britain, where substantial natural outcrops are absent.

The chalk outcrops along the north coast of Ireland are rich in flint and are assumed to have been intensively exploited during prehistory (Briggs 2001, 42). At Mount Sandel, Coleraine, evidence for early Mesolithic habitation of Ireland was discovered on a bluff overlooking the River Bann (Woodman 1985). At Mount Sandel Lower, Collins found that the flint used for toolmaking is very high quality, exhibiting a colour range consistent with sources along the Antrim coast (1983, 6). This is also the case at Mount Sandel Upper, excavated by Woodman, where flint from the north coast was preferentially used over the pebbles found in the glacial deposits surrounding the site (Woodman 1985, 151-5). At both Mount Sandel Upper and Lower, knapping debris indicated that the majority of the processing took place on-site, with nodules or semi-prepared blanks being brought to the site from the coastal sources (Tolan-Smith 2008, 150).

Outcrops of 'clay-with-flints' on the chalk downs of southern England also provide evidence for early Mesolithic exploitation. The early Mesolithic site of West Hill, Pyecombe, West Sussex is located on a clay-with-flints outcrop and is a palimpsest of the low-intensity, seasonal exploitation of flint nodules found on or near the surface in this area (Butler 2001, 16). In Hampshire, the early Mesolithic occupation was focused on the areas of clay-with-flints, whereas chalk flint was more frequently utilised in the Weald (Care 1982, 273-75). Flint procurement in the Weald during the early Mesolithic was focused almost exclusively on the chalk flint occurring near the coast; nodules or semi-processed blanks were brought from the source to the site, where most of the knapping took place (Care 1982, 273).

It would appear from the use of raw material in the Vale of Pickering that proximity and quality were not the deciding factors for early Mesolithic hunter-gatherers. The early Mesolithic site of Seamer C revealed eleven discrete flint scatters that evidenced preferential use of secondary flint sources; grey-white Wolds flint and brown/grey beach flint (Conneller & Schadla-Hall 2003, 90). Complete nodules were transported from the coast to Seamer C, where they were reduced and used for tool-making (Conneller 2011, 100). The beach flint was preferentially used over the Wolds flint at most sites in the Vale of Pickering (Conneller 2007, 233); the most striking feature of the Vale of Pickering scatters is their dissimilarity to each other, both in terms of choice and quality of raw material (Conneller & Schadla-Hall 2003, 100).

The worked stone assemblage at Howick, Northumberland was comprised mainly of flint, the majority of which was manufactured from pebbles procured from nearby beaches - these were imported whole and reduced on-site (Waddington *et. al.* 2003, 8). A similar strategy was employed at Fife Ness, Fife, where pebbles from the local gravels were collected and brought to the site, prior to reduction (Wickham-Jones & Dalland 1998, 15). The early Mesolithic use of

the site at Toome Bridge, Northern Ireland saw the use of flint pebbles from the local gravels; the evidence for importing superior quality flint from the coast is not evident (Woodman 2010, lxi).

In areas where flint was entirely absent, there are indications that it was imported. Excavations at Ulva Cave, Mull, Western Scotland, revealed flint debitage despite the absence of flint sources on the island (Bonsall *et. al.* 1992, 7; 1994, 9). As primary sources of flint are not found in Scotland, the flint found on Ulva was obtained from beach pebbles, which have a limited distribution on the Western Isles - restricted to the west-facing coasts of Islay, Colonsay and Iona (Marshall 2000, 77).

2.4 The British and Irish Neolithic

The Mesolithic-Neolithic transition in Britain and Ireland has generated a huge corpus of literature and is the subject of vociferous debate (see Armit & Finlayson 1992; Cummings & Harris 2011; Finlayson & Warren 2010; Schulting 1998 and 2004; Schulting & Richards 2002; Whittle & Cummings 2007). It is beyond the scope of this thesis to investigate the nature and timing of this transition, or discuss the various strands of evidence that are referenced in archaeological discourse.

A recent dating programme undertaken by Whittle, Healy and Bayliss (2011) has attempted to provide clearer dates for the introduction of the Neolithic using a Bayesian statistical framework. This research has dated the first appearance of the Neolithic package in southeast England between 4100 - 3900 cal BC, represented by Carinated Bowl pottery, monumental construction, timber houses, and flint mines (Bayliss *et. al.* 2011, 833). The early Neolithic in Scotland is dated c.3800 cal BC, with dates suggesting that it may have taken several centuries for farming to spread to the north of Scotland (Bayliss *et. al.* 2011, 822-38). The arrival of

farming in Ireland is more complex, as the majority of dates seem to suggest a date of c.3800-3700 cal BC however the enclosure at Magheraboy predates this by 200 years, and a cattle bone found at Ferriter's Cove would appear to be a pre-Neolithic introduction (Bayliss *et. al.* 2011, 837-40; Tresset 2003).

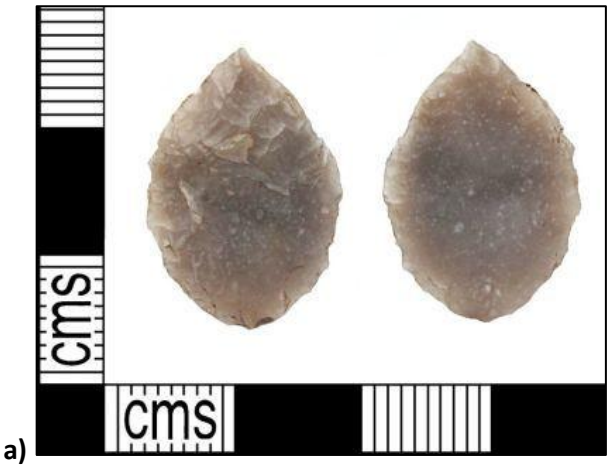
2.4.1 Flint tool industries

In Ireland, the lithic technology associated with the early Neolithic appears to be distinct from the preceding Mesolithic toolkit, with no evidence of a transitional lithic industry (Kador 2010, 147). However some early Neolithic assemblages echo late Mesolithic technology, with butt-trimmed forms excavated from the Antrim sites of Thornhill, Donegore Hill, Lyles Hill and Squires Hill; Nelis states that there is no reason to consider these artefacts as representing residual later Mesolithic activity (Nelis 2004, 171).

Woodman's review of the early Neolithic in Ireland proposes a set of diagnostic artefact types; including large, leaf-shaped arrowheads, convex end scrapers, and elongated, plano-convex knives, utilising different methods of production, specifically pressure flaking, increased use of soft hammer percussion and multi-platform cores with different platform types (Woodman 1994). However, the early Neolithic in Ireland appears not to include sickles or insets (Warren 2006, 43). Flaked flint axes were also produced during the Neolithic in Ireland, as they had been during the Mesolithic, although they are heavily outnumbered by axes made from other lithologies, particularly porcellanite (Mandal *et. al.* 1997, 757). The Irish Stone Axe Project has undertaken a comprehensive archaeological and petrological survey of stone axes from Ireland, and found that flint - despite large, good quality deposits in the Cretaceous chalk of the north Antrim coast - was not widely used for axes, due largely to its brittle structure, and the greater resilience of porcellanite (Cooney & Mandal 1995, 971). Flint axes are found more

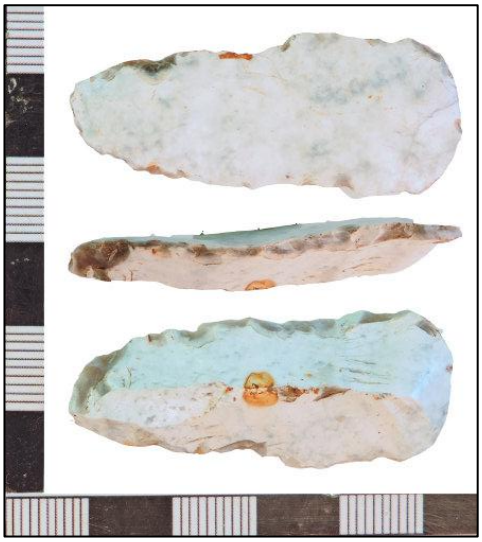
frequently in Ulster, but only comprise 10% of the total number of known axes (Cooney *et. al.* 1999, 20).

The importance of projectile points is evidenced from Ballyharry, Antrim, where leaf (Figure 2.11), lozenge and laurel-leaf arrowheads are found in association with micro-debitage and trimming flakes (Moore 2004, 144). Analysis of the early Neolithic assemblages from Belderg Beg, north Mayo, provide evidence for the widespread use of bipolar knapping, and it has been suggested that this approach was integral from the early Neolithic onwards (Driscoll 2010, 17). However lithic analysis of tools from Island Magee, Antrim, found that multi-platform, narrow blade cores were typical of early Neolithic activity (Duffy *et. al.* 2000, 22).



a)

b)



c)

Figure 2.11 - Early Neolithic flint tool assemblage (a: leaf-shaped arrowhead, North Yorkshire (PAS 2013d), b: end scraper, Dorset (PAS 2013e), c: plano-convex knife, Lincolnshire (PAS 2013f)) (all scale bars in cm)

The early Neolithic in Ireland also saw the widespread use of scrapers. In late Mesolithic contexts, scrapers of any kind are “exceptionally rare” (Woodman 1978, 78), however during the early to middle Neolithic scrapers become ubiquitous. At the early Neolithic sites of Donegore and Lyles Hill, Co. Antrim, scrapers dominated the excavated assemblages (Nelis 2003, 206-16). Although not found in the earliest Neolithic contexts, hollow scrapers seem to appear during the middle of the early Neolithic period in Ireland and are regarded as an indigenous invention (Kimball 2000, 4). Hollow scrapers are not found exclusively in Ireland, as examples have been found on the Cumbrian coast, north Wales and the Western Isles (Edmonds 2005, 38).

The early Neolithic in Britain sees the continuation of blade production (Finlay *et. al.* 2002, 109), as well as retouched pieces that are broadly similar to those found in Ireland; leaf-shaped arrowheads, plano-convex knives, as well as a range of convex scrapers (Warren 2006, 27). Flakes are predominant in the southern British Neolithic (Edmonds 2005, 37), whereas lithic technology in Scotland is based around the production of blades, although the Levallois technique allowed for the creation of flakes and blades from the same core (Brophy & Sheridan 2012, 71). The Neolithic in Scotland shows some degree of continuity from the late Mesolithic, as lithic technology was focused on blade production (ScARF 2013). Serrated flakes are less common in Scotland, presumably due to the focus on blade production (Edmonds 1997, 37). The range of lithic tools in the Scottish early Neolithic is broadly comparable to those found in southern Britain and Ireland, although they are not as fully understood for the Scottish early Neolithic (Noble 2006, 20).

There are a number of core types in use throughout the early Neolithic, including single platform, opposed platform and bipolar core, creating narrow flakes and blades of regular thickness; however bipolar cores are more frequent in areas lacking substantial flint deposits,

such as western and northern Britain (Edmonds 1995, 32). In Scotland, where flint is found mainly as redeposited/secondary pebbles, bipolar knapping forms an important component of the early Neolithic assemblages (Warren 2006, 27). The introduction of invasive retouch (Figure 2.12) during the early Neolithic allowed for the creation of sophisticated projectile points and cutting implements, such as leaf-shaped arrowheads and plano-convex knives (ScARF 2013). In Scotland, direct soft/medium percussion is common although in some cases the cortex was removed using hard hammer percussion (Warren 2006, 37).

Sites such as Charlwood and North Park Farm (both in Surrey) demonstrate that, despite the abundance of local flint, the raw material was being extensively worked, with core rejuvenation pieces and well-worked cores showing considerable knapping skill (Leivers 2004, 2).

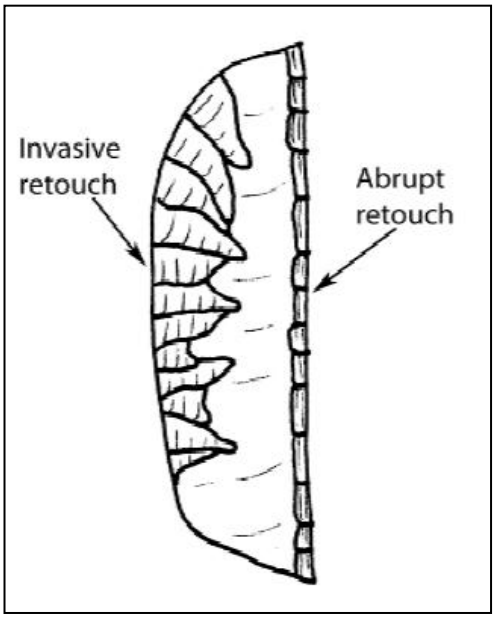


Figure 2.12 - Invasive retouch on flint blade (Tees Archaeology 2013)

Perhaps the most iconic tool type of the British Neolithic are polished stone axes, which were made from various lithologies including flint (Figure 2.13), tuff, quartzite and exotic materials

such as continental jadeite and porcellanite from northern Irish sources. The establishment of flint mines in Sussex and Wessex were one of the first features of the Neolithic in Britain (Bradley 2009, 37). Flint axes are frequently recovered from early Neolithic sites in Britain, with centres of production focused on the superior quality mined flint in the south of England (Gardiner 1990, 119). The sources of raw material for stone axes have been studied in detail, and objects matched to specific locales (Clough and Cummins 1979; 1988).

The study conducted by Bradley & Edmonds (1993) into the axe production site at Great Langdale investigated not only the site itself but the process behind, and meaning of, the creation and movement of axes during the early Neolithic. Their study, inspired by the petrological examination carried out as part of Stone Axe Studies I & II (Clough & Cummins 1978; 1989), looked further into the meaning behind the movement of axes throughout Neolithic Britain and Ireland. The discovery of stone axes in areas of Britain or Ireland with a local supply of good-quality flint was an indication that the functional or mechanical properties of these artefacts were not priorities. The perception of the Neolithic is based almost exclusively on the economic and social changes that occurred, however it is wrong to assume that people in the past considered trade and exchange along formal economic lines (Hodder 1982, 202). There is also no reason to assume that axes were viewed in the same light throughout the Neolithic.

The difference in treatment of axes made from local and non-local material is significant. Bradley & Edmonds observe that axes found in the Yorkshire Wolds that are made of local raw material are predominantly unpolished, whereas axes made from non-local material were always polished (1993, 49). The difference in treatment indicates that local or non-local raw material seemingly warranted specific action. Understanding artefacts is to account for patterns of association and avoidance, as well as the symbolism inherent in the piece (Hodder

1982, 209). Avoidance of flint for axe-making in certain areas, or at least preference for imported axes, indicates to archaeologists that a focus along purely economic lines would not be useful as function and availability of raw material (flint) was passed over in favour of exotic, strange, yet often mechanically weaker material.

Figure 2.13 - Early Neolithic polished flint axe, Norfolk (PAS 2013g)

The introduction of agriculture represents a drastic change to the way of life for the inhabitants of Britain and Ireland. Analyses of the lithic technologies present during the early

Neolithic have been somewhat side-lined in favour of monuments, economy and ceramics; the apparent uniformity of lithic tools during this period has received little explicit attention (Warren 2006, 43).

There are a number of subtle changes in lithic technology that occur throughout the Neolithic period; these changes are evident in both the types of tools being manufactured and the methods used to create them. The Neolithic in Britain is divided into early and late; the late Neolithic begins c.3000 cal BC and continues until the beginning of the Bronze Age, c.2500 cal BC (Whittle 1999, 59-60). In Ireland, the stages of the Neolithic are based on changes in monumental architecture and pottery styles (Cooney 2000, 17). The division of the Neolithic in Ireland is not relevant in terms of lithic technology as there are no specific middle Neolithic lithic technologies. The late Neolithic/early Bronze Age transition is not clear-cut in terms of lithic technology. Distinguishing between late Neolithic and early Bronze Age flintwork is often difficult (Parker-Pearson 2007, 78).

There are a number of tool types that are found in both the late Neolithic and the early Bronze Age, specifically thumbnail scrapers, flaked knives and barbed and tanged arrowheads. The beginning of the Bronze Age is most clearly defined, with regards to lithics, by a general decline in knapping skill in the production of non-prestige objects (Humphrey & Young 1999, 58), however there is a marked increase in the level of skill displayed in the creation of prestige objects such as flint daggers (Ballin 2002, 25). The decline in knapping skill is evidenced by the gradually shorter and thicker blades, as well as an absence of core preparation and maintenance (Ballin 2002, 24).

The invasive retouch which had been used to finish the leaf-shaped arrowheads and plano-convex knives of the earlier Neolithic began to be phased out, with a move towards more

minimal retouch (Nelis 2004, 171). The hollow scrapers which emerged in the middle of the Irish early Neolithic became widespread, becoming less frequent towards the end of the period, and being replaced by thumbnail scrapers (Figure 2.14) by the late Neolithic/early Bronze Age (Nelis 2004, 165-8). Examples of invasive retouch from the early Bronze Age appear to be functional rather than aesthetic, and retouch is applied perfunctorily and sparsely (Bradley & Leivers 2009, 17).

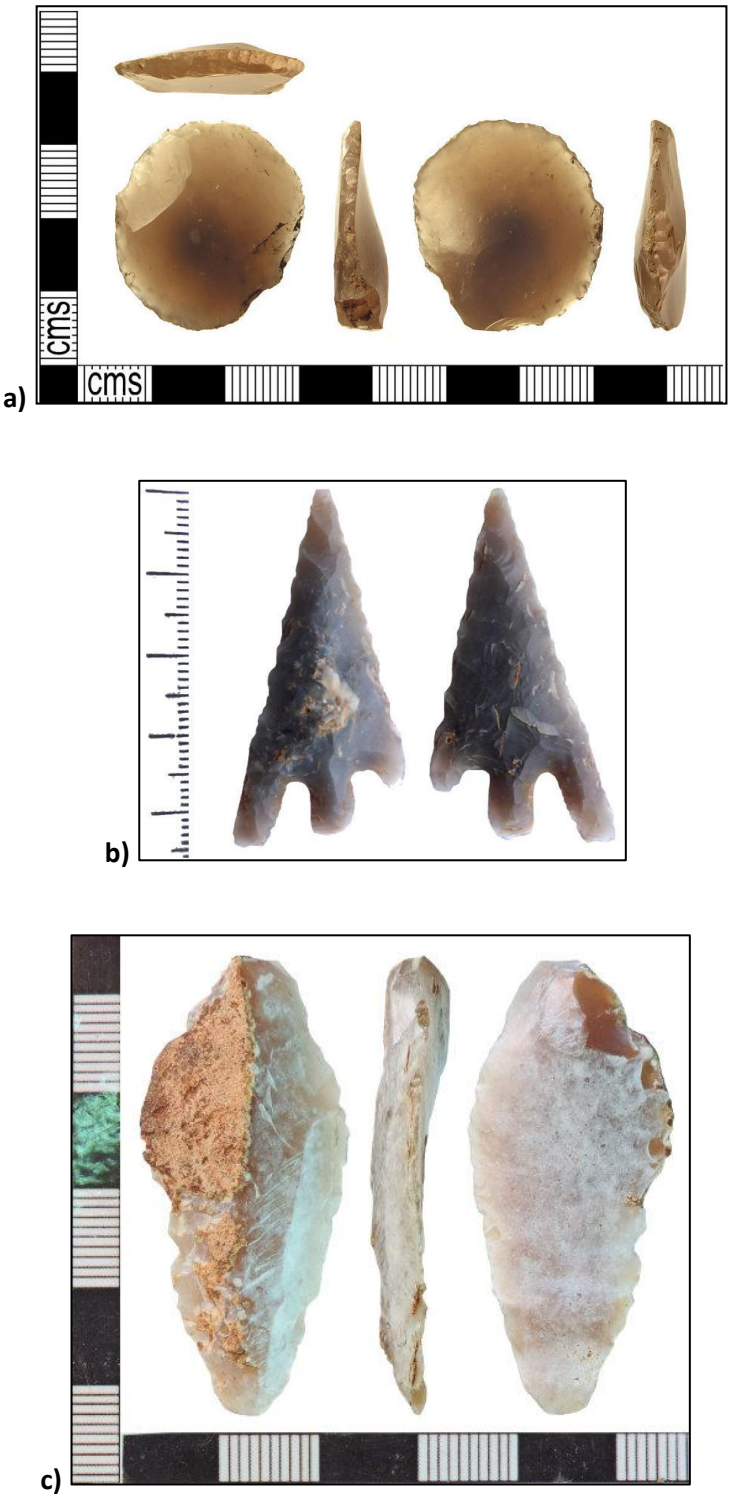


Figure 2.14 - Late Neolithic assemblage (a: thumbnail scraper, Isle of Wight (PAS 2013h), b: barbed-and-tanged arrowhead, Lincolnshire (PAS 2013i), c: flaked knife, Lincolnshire (PAS 2013j)) (scale bars in cm)

The lithic assemblage from Townparks, Antrim, provides a small diagnostically late Neolithic group of artefacts, including an oblique arrowhead and horseshoe-shaped end-scraper (Ballin and Will 2005, 15). These tools were produced from flakes from multi-platform and/or disc cores, such as those found at Island Magee, Antrim (Duffy *et. al.* 2000, 22). The use of bipolar cores did continue in some areas through the late Neolithic; the excavations at Skreen 2, Meath, revealed a late Neolithic post-built structure with associated lithic remains, manufactured on flakes from bipolar cores (O'Neill & O'Hara 2008, 6). Early Bronze Age material from Ireland includes small disc scrapers, which comprised half the classifiable scrapers from Belderg Beg, Mayo (Driscoll 2010, 9). The site at Oakgrove, Derry, revealed two well-made flint blades dating to the early Bronze Age (Chapple 2008, 28). Bipolar core technology was widespread in Ireland from the early Neolithic onwards, although its extensive use in the Bronze Age is such that it has been described as a 'temporal marker' for the whole Bronze Age in Ireland (Driscoll 2012, 14).

In Britain, the change in lithic technology during the Neolithic is more pronounced. The late Neolithic in Scotland saw a technological watershed, with blades featuring prominently in the earlier Neolithic (as they did in the late Mesolithic) but a mixed blade/flake technology during the late Neolithic (Suddaby & Ballin 2010, 40). Through the later Neolithic, flakes became larger and squatter, and blades became gradually wider (Hart 2006). Core technology also changed towards the end of the Neolithic period, with the introduction of a Levallois-like technique. This approach involved the controlled, extensive preparation of a core in order to detach broad flakes, which served as blanks for arrowheads and serrated pieces (Edmonds 1995, 89). A late Neolithic assemblage was excavated from Spring Road Municipal Cemetery, Oxfordshire, and contained a mixture of single-, multi- and Levallois-type cores, as well as diagnostically late Neolithic chisel arrowheads, serrated flakes and backed knives (Lamdin-

Whymark 2008, 33). Barbed and tanged arrowheads are also a diagnostic flint tool type of the later Neolithic (Figure 2.14), and appear to be more frequent in central and southern England, although they are also found in Wales (Field 2008, 48). Thumbnail scrapers are also an important feature of late Neolithic and early Bronze Age assemblages (Figure 2.14).

The early Bronze Age lithic tools in Scotland show continuity with the late Neolithic technologies. Late Neolithic and early Bronze Age assemblages in Scotland are generally small, with an emphasis on flake production, getting gradually shorter into the Bronze Age (Suddaby & Ballin 2010, 40). Diagnostic early Bronze Age flint tools in southern Britain also demonstrate the similarities with late Neolithic assemblages; barbed and tanged arrowheads, backed knives, and thumbnail scrapers, although these pieces are often residual, with large assemblages occurring in the later Bronze Age (Cramp & Leivers 2010, 52-3). Securely dated assemblages from the Bronze Age tend to be discovered in funerary contexts; these often contain pieces showing highly skilled workmanship (Healy & Harding 2004, 176; Leivers 2004, 6). An early Bronze Age burial excavated near Amesbury, Wiltshire, in 2002 was perhaps the richest found in Britain (Fitzpatrick 2002, 630). The occupant obtained the moniker 'the Amesbury Archer', due to the 16 finely-crafted barbed-and-tanged arrowheads found in his grave (Figure 2.15) (Scarre 2007, 123).

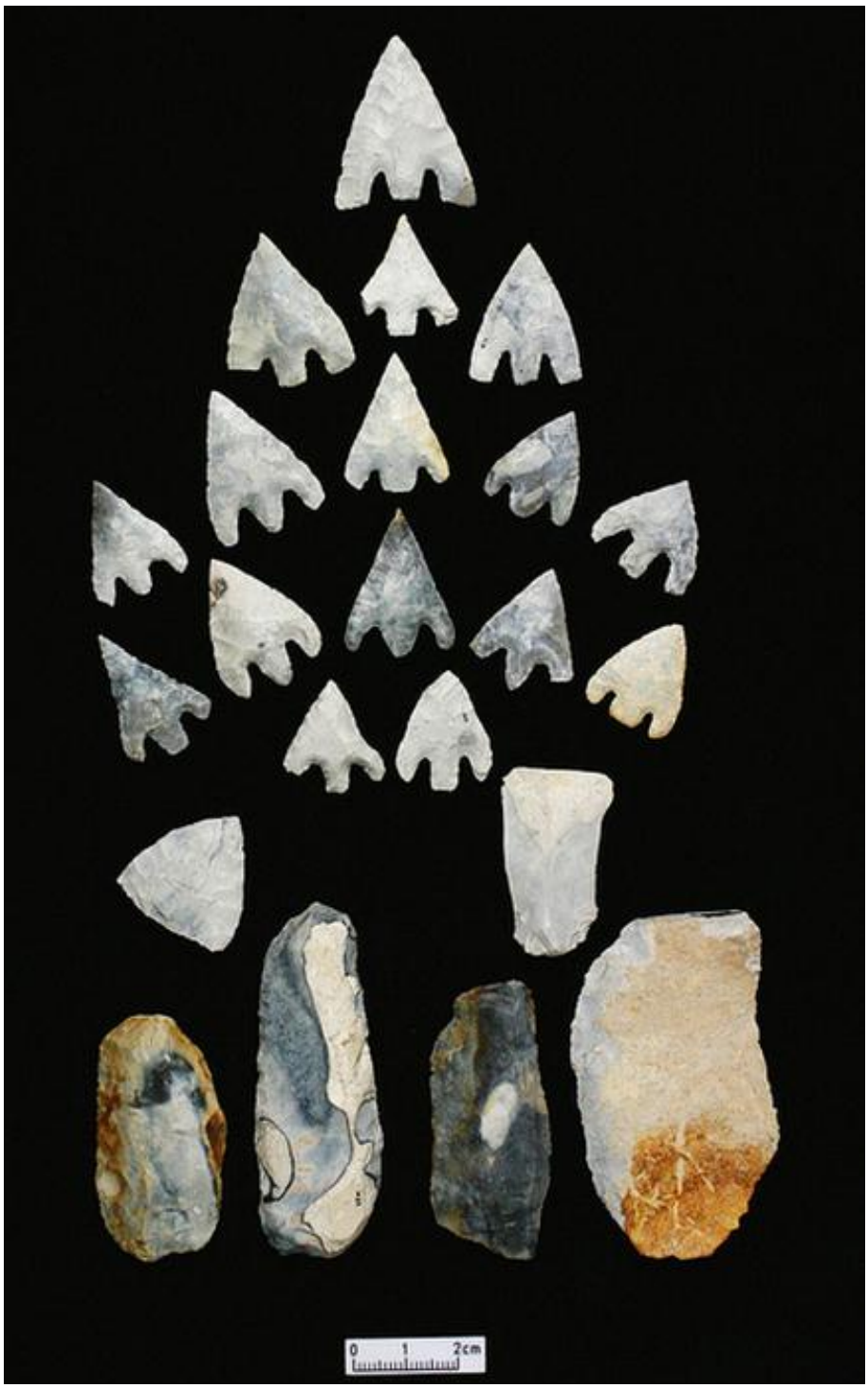


Figure 2.15 - Flint grave goods from the burial of the Amesbury Archer (Wessex Archaeology 2013)

The early Neolithic witnessed the beginning of large-scale flint mining; this development was inextricably linked to the demand for axes, as large quantities of high-quality flint is required to produce an axe (Price 2015, 137). Axes continued to be manufactured into the later Neolithic and early Bronze Age (Ford *et. al.* 1984, 166), although it appears their presence is linked to more than just raw material availability. Kirk has noted that flint axes are notably rare on the Scilly Isles, despite the presence of large nodules that would be suitable for axe production (Kirk 2004, 236). Other diagnostically late Neolithic implements made their way to the Scilly Isles, including barbed and tanged arrowheads, but axes appear to have a very limited distribution (Kirk 2004, 236).

2.4.2 Exploitation of primary and secondary deposits of flint in the British and Irish Neolithic

The most obvious exploitation of primary deposits in the Neolithic was the sinking of mines into the flint-rich chalk that lies underneath large areas of Wessex and Sussex (Figure 2.16) (Leivers 2004, 1). These areas are peppered with mineshafts, indicating that intensive exploitation took place when suitable flint was located. This flint, which occurs in large nodules or extensive tabular seams, was heavily exploited for axe production during the early Neolithic (Gardiner 1990, 120). The early Neolithic sites of Haldon and Hembury (both in Devon) made extensive use of flint from Beer, which was brought to site in nodular and semi-processed form (Care 1982, 277).

Similarly, in the north of Ireland, the primary deposits of flint along the Antrim coast were exploited for the production of flaked flint axes; however the assemblages from Thornhill (Derry) and Ballynagilly (Tyrone) appear to indicate a relative paucity of raw material, with tools showing evidence of frequent rejuvenation (Nelis 2004, 159). Axehead manufacture in

the north of Ireland appears to have taken place at specific locales, such as Ballyharry and Cloughers (both in Antrim) (Smyth 2006, 240).

The early Neolithic site at Auchategan, Scotland, provides a lithic assemblage comprised of flint, quartz and pitchstone. The quartz is thought to be local, but the pitchstone was imported from Arran, and the fresh, chalky cortex of the flint indicates that it came from primary deposits, most likely the Antrim coast (Ballin 2006, 16).

Overall, the primary deposits of flint in Britain and Ireland appear to have been exploited to meet the demands of axe manufacture. The phenomenon of flint mines throughout the south of England is not apparent in the north of Ireland. This is likely to be due to the layers of basalt which cover the flint-bearing chalk deposits in the north of Ireland (Shelton 1997, 123), as well as the hardness of the chalk which have been baked by the basalt (Briggs 1986, 185).

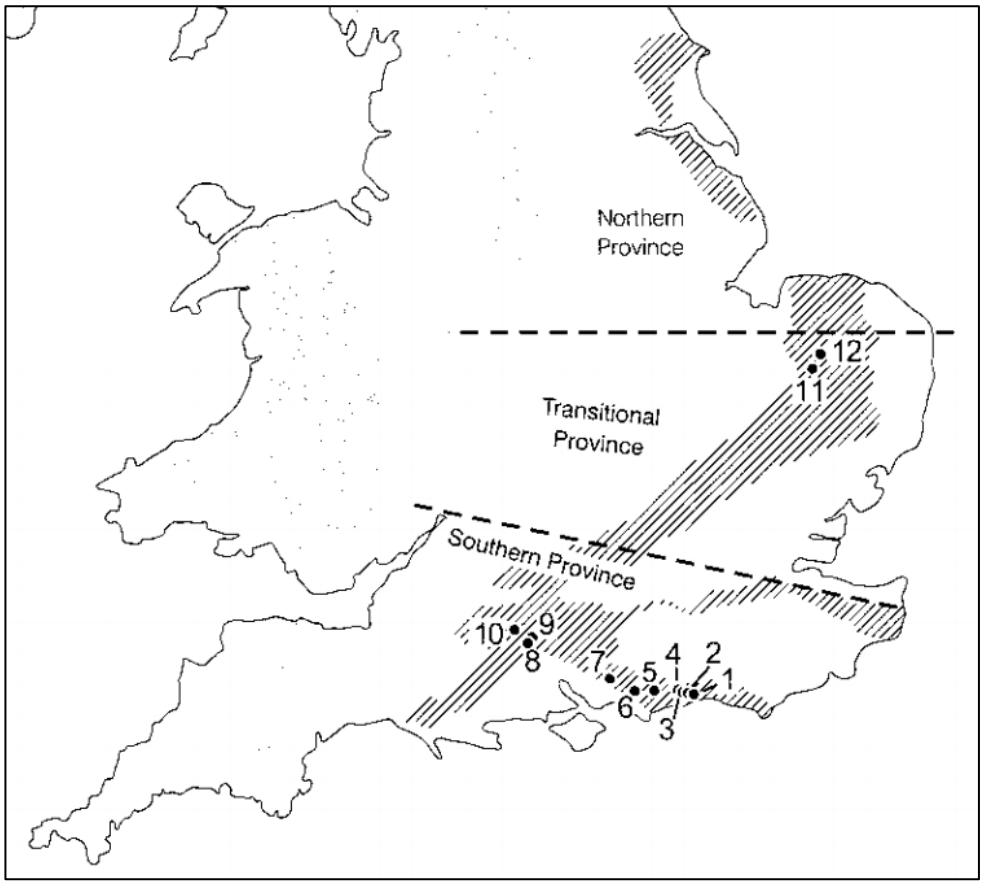


Figure 2.16 - Known Neolithic mines in mainland Britain (1: Cissbury; 2: Church Hill/Tolmere Pond; 3: Blackpatch; 4: Harrow Hill; 5: Long Down; 6: Stoke Down; 7: Nore Down; 8: Easton Down; 9: Martin's Clump; 10: Durrington; 11: Grimes Graves; 12: Buckenham Toft) (after Barber et. al. 1999, ix)

During the late Neolithic, axe production was focused on large scale mining of various lithologies. Recent Bayesian analysis of C^{14} dates identifies flint mining as occurring in Sussex in the 40th century cal BC, meaning that flint mining was one of the earliest Neolithic innovations in the southeast of England (Healy *et. al.* 2011, 261). Towards the later Neolithic in Sussex, the focus shifts to surface deposits, particularly clay-with-flints (Gardiner 1990, 119). Mining did not end completely, however, as Grime's Graves was established during the latter part of the Neolithic and continued into the Bronze Age (Edmonds 1995, 129). The flint mines in Sussex

continued to be visited, and although there is no evidence for continued mining after the early Neolithic, flint from surface spoil and upper fills of the shafts was utilised in the late Neolithic (Gardiner 1990, 120).

In the north of Ireland, exploitation of the large flint deposits on the Antrim coast continued into the late Neolithic and early Bronze Age. The use of this raw material is inferred from a number of sites. Townparks, Antrim, contains a late Neolithic assemblage made from two distinct kinds of flint; grey flint artefacts found on site are interpreted as having come from the coast, whereas the brown flint is local, erratic flint (Ballin & Will 2005, 14). The assignation of source based on colour is difficult; however the mid-late Neolithic site at Goodland, Antrim, had access to primary deposits of flint as the size of tools manufactured required sizeable nodules, which are found in abundance on the coast (Nelis 2004, 168).

During the early Neolithic in Britain and Ireland, secondary sources of flint appear to have been more extensively exploited. This may well be due to the relative lack of primary deposits, although it has been suggested that sources of high quality flint (such as mined flint), may have come under some degree of social control and access was restricted (Care 1982, 270).

Although the suggestion of restricted access to flint sources is hypothetical and unproven, there are a number of areas in the north of Ireland that appear to be unusually dependant on secondary sources. In a survey of the Lough Swilly environs, Kimball found that the late Mesolithic lithic assemblages were manufactured on flint imported from the Antrim coast, whereas the early Neolithic material was made from the local erratic flint (2000, 46). Similarly, the sites of Donegore Hill and Lyles Hill (both in Antrim) made extensive use of local beach pebbles, despite the relative proximity of the flint-rich Antrim coast (Nelis 2003, 206).

In northern Britain, there are limited sources of flint that are suitable for manufacturing large tools such as axes. The Neolithic axes found in Scotland are made of a variety of lithologies; local sources were used, including felsite quarried from the Shetland Islands as well as bloodstone from Rhum and pitchstone from Arran (Ballin 2007). The Buchan Ridge gravels contain flint pebbles, and are assumed to have been extensively exploited throughout prehistory (Suddaby and Ballin 2010, 24). These gravels would have provided an excellent source of flint during the early Neolithic, although it does not appear to have travelled widely within Scotland if Antrim flint was being imported to meet demands on the west coast (Ballin 2006, 16). There is some evidence to suggest that flint was imported from the Yorkshire Wolds during the latter part of the early Neolithic (Ballin 2011, 27).

Evidence of exploitation of secondary sources was also inferred from the excavations at Cheviot Quarry, Northumberland. The early Neolithic assemblage from this site has been manufactured from flint sourced from pebbles found within local boulder clay, although larger pebbles and nodules are thought to have been imported from the Yorkshire Wolds, approximately 160km south of the site (Waddington 2006, 7).

The use of secondary sources of flint continued into the late Neolithic. The site of Townparks, Antrim, made extensive use of local erratic flint available from the surround glacial deposits, which was supplemented by imported flint from the coast (Ballin & Will 2005, 14). The interior of Scotland is lacking in flint sources, with the closest raw material located at Buchan Ridge (Aberdeenshire) or Antrim. While the Buchan Ridge gravels continued to be exploited throughout the late Neolithic (ScARF 2013), there is evidence to suggest that flint was being imported from the Yorkshire Wolds, with trade networks stretching as far north as Orkney (Ballin 2011, 38).

In the early Bronze Age in Scotland, flint is used as a supplementary material with quartz, baked mudstone and chert forming the majority of many assemblages (ScARF 2013). This may be due to the lack of accessible flint deposits, which are restricted to Aberdeenshire and coastal regions. There are exceptions to this, as the site at Stoneyhill Farm, Aberdeenshire, revealed a lithic assemblage comprised almost entirely of flint (c.99%), likely sourced from the Buchan Ridge gravels (Suddaby & Ballin 2010, 24).

In the flint-rich regions of southern Britain, raw material continued to be sourced from gravels and clay-with-flints in the early Bronze Age (Leivers 2004, 1). Boulder clay and river gravels were utilised in Northamptonshire, although there is also evidence for the scavenging of flint eroding from barrows (Ballin 2002, 8). Clay-with-flints were especially significant sources throughout prehistory, with Mesolithic to Bronze Age exploitation of the clay-with-flints deposit at East and West Hills, Pyecombe (Butler 2001, 7).

The choice of secondary sources of flint, as opposed to superior-quality primary deposits, appears counter-intuitive. However, it is suggested that the constraints of an agricultural economic base led to a more ad-hoc approach to raw material collection (Kimball 2000, 4). This may explain the choice of secondary sources at Durrington, despite the proximity of primary deposits. At Durrington, local surface flint was used, despite frequent internal flaws and varying quality (Chan 2010, 50).

The Neolithic period represents a sea change in British and Irish prehistory. The lithic industries present during this time differ considerably from the preceding late Mesolithic toolkits, but do not differ significantly within themselves. Flint was used throughout the Mesolithic and Neolithic for toolmaking and was the dominant lithology utilised in large areas of Britain and Ireland. There are subtle changes that occur throughout the Neolithic period; including

changes in scraper and arrowhead morphology, changes in core technology, and the advent of large-scale flint mining in the south of England. Due to the inherent durability of flint, and the observable changes in typology throughout the Mesolithic and Neolithic, archaeologists can be confident in understanding the use and sourcing of this material. The transition between the Neolithic and Bronze Age is less distinct. Confirmation of early Bronze Age lithics often relies on securely dated contexts, such as burials, rather than typology. There was a gradual decline in knapping skill during the Bronze Age, however prestige items such as daggers and flaked knives continue to be manufactured, albeit rarely.

As was demonstrated for the Mesolithic period, the choice of raw material during the Neolithic can appear paradoxical. Exploitation of the Antrim flint sources appears to dwindle as the Neolithic progressed; the flint mining in the South Downs ceased in the middle of the Neolithic, only to begin again in East Anglia and continue into the Bronze Age at Grime's Graves. It has been suggested that productive; high-quality sources of flint came under some degree of control during the Neolithic (Care 1982, 269-70), although evidence to support this claim is not forthcoming. The traditional view of the Neolithic period as sedentary and territorial (Armit & Finlayson 1992, 667) would appear to support the hypothesis that flint mining was a strictly controlled activity. However there are difficulties in finding supporting archaeological evidence for territoriality, particularly since the chronology of certain mines are represented by one C^{14} date (Blackpatch, Church Hill, and Easton Down) (Barber *et. al.* 1999, 68), making it very difficult to prove duration of use.

Secondary sources of flint continued to be extensively used throughout the Neolithic and early Bronze Age. This is to be expected, as primary deposits of flint are geographically restricted. However, as in the Mesolithic, there appears to be non-utilitarian reasons for the use of certain sources. During the late Neolithic in Scotland, flint was imported from the Yorkshire

Wolds, despite the proximity of the Buchan Ridge gravels in Aberdeenshire and pebble flint on the Inner Hebrides. It is likely that the flint imported from Yorkshire was valued as an exotic or symbolically important material - just as axes of foreign lithologies were traded and valued across Britain and Ireland. During the early Bronze Age, a range of raw materials were used, with flint playing a much less prominent role in toolmaking.

2.5 Summary

The development of archaeological thought during the twentieth century has profoundly changed the nature of the discipline as a whole and has provided the contemporary archaeologist with a rich corpus of debate, discussion, and data. The approaches to trade and exchange as outlined in this chapter have become increasingly more sophisticated, both ideologically and analytically. The culture-historical zeal for categorisation and typological division is now viewed as naïve and limited, however there is hardly an archaeological publication that exists today that does not rely, at least in part, on chronological, typological, or classificatory schemes established during the early twentieth century. Similarly, the processual obsession with data and scientific analysis was rightly criticised for its narrow focus on quantification, but the data obtained underpins our understanding of many aspects of past societies. Both culture-history and processual archaeology were necessary steps in the evolution of archaeological thought, and the value of these approaches is evident in their integration in present-day narratives. The fusion of these with the wealth of post-processual perspectives on offer today allows us to approach the past in a holistic manner and view prehistory through a multitude of viewpoints.

3. GEOLOGY OF FLINT AND A HISTORY OF STONE SOURCING

This chapter will describe the geological processes that lead to the formation of flint. It will also cover the occurrence of flint sources in Britain and Ireland, as well as the enormous variation in the appearance of flint, and the implications of this for geochemical provenancing. This chapter will also review the recent literature regarding scientific approaches to sourcing artefacts of various lithologies, and the relevance of this research for this study.

3.1 Formation of flint

Flint was used throughout prehistory for tool manufacture (see previous chapter). It occurs as nodules or tabular layers in chalk formations, which were quarried or mined to extract the flint. Flint can also be found as scattered pebbles or gravels where the parent chalk has been eroded and weathered, or disturbed through glaciation. The exact process of flint formation remains a subject of debate; evidence from deep-sea drilling has allowed geologists to infer details about flint formation (Lindgreen & Jakobsen 2012, 11-2), although the cores drilled from the sea bed only provide snapshots in the complex diagenesis of flint (Kolodny & Epstein 1976, 1208).

3.1.1 Chalk

The chalk cliffs and downlands that characterise the south of England are remnants of the Late Cretaceous period, which lasted from 100-65 million years ago (Table 3.1) (Goudie 1993, 9). From the mid-Cretaceous onwards, global sea levels rose and submerged vast swathes of land.

EON	ERA	PERIOD	EPOCH	DATES (10^4 YEARS BP)
Phanerozoic	Cenozoic	Quaternary	Holocene	0.01
			Pleistocene	1.8
		Tertiary	Pliocene	5
			Miocene	23
			Oligocene	38
			Eocene	54
			Palaeocene	65
	Mesozoic	Cretaceous		144
		Jurassic		208
		Triassic		245
	Palaeozoic	Permian		286
		Pennsylvanian		325
		Mississippian		360
		Devonian		410
		Silurian		440
		Ordovician		505
		Cambrian		544
Proterozoic				2500
Archaen				3800
Hadean				4500

Table 3.1 - Divisions of geological time (*after McGraw-Hill 2003, 418*)

The warm, clear, shallow seas that covered much of Europe during the Cretaceous period were occupied by calcareous organisms, such as coccolithophores, whose calcium-carbonate plates formed the nannofossil ooze that blanketed the Cretaceous seabed (Rawson 2006, 387). This nannofossil ooze accumulated and cemented, becoming the chalk (Brenchley & Rawson 2006,

7). The margins of the large, shallow basins where the chalk formed shifted during the Cretaceous period through eustatic change; the late Campanian maximum transgression left little available land surface (Hancock 1975, 528). Deposition of chalk occurred over enormous areas during the Late Cretaceous, with chalk formations stretching from Ireland to Kazakhstan (over 7,000km) (Rawson 2006, 387). The Cretaceous period is divided into Early and Late (or Lower and Upper), and these are further subdivided based on 12 distinct layers based on variations in biostratigraphy (Table 3.2) (Gradstein *et. al.* 2012, 794).

System	Series	Stage	Age (Ma)
CRETACEOUS	Late	Maastrichtian	66-72
		Campanian	72-83.5
		Santonian	83.5-86
		Coniacian	86-89
		Turonian	89-94
		Cenomanian	94-100
	Early	Albian	100-113
		Aptian	~113-~125
		Barremian	~125-~129
		Hauterivian	~129-~133
		Valanginian	~133-~140
		Berriasian	~140-~145

Table 3.2 - Cretaceous stages (after Gradstein *et. al.* 2012, 794)

These subdivisions are of relevance for this study as the chalk that formed at different points during the late Cretaceous has a variable quantity of flint bedding, as well as differences in the form of flint present.

Cretaceous chalk deposits in England are divided into three distinct provinces; Northern, Southern, and Transitional (Figure 3.1) (Hopson 2005, 2). The chalk of the Northern Province is harder than that in the Southern Province, indicating that it may have formed under deeper water (Toghill 2000, 150). The Northern and Southern provinces are well-defined based on differences in rock type and fossil species; the Transitional province is poorly defined by comparison and contains a mixture of Northern and Southern rock types and fossil species (Mortimore *et. al.* 2001, 7). The chalk in the Transitional province is also much thinner than its Northern or Southern counterparts; Northern Chalk can be found in deposits up to 500m thick, whereas the Southern Chalk can be up to 150m thick (Toghill 2000, 150). The stratigraphical distribution of flint and the type of flint found in the Northern Province is totally different to that found in the Southern Province; the Northern Chalk is hard and well-bedded, whereas the Southern Chalk is massive (meaning unbroken by fissures, bedding features, or cracks, more homogeneous in appearance) and soft (Mortimore & Wood 1986, 8). The chalk found in the north of Ireland is exceptionally hard, due to heating and compaction from the overlying basalt (Briggs 1986, 185).

The Northern Chalk province is more closely related to the chalk found in the Boreal Realm (northern Europe, including Germany and Scandinavia), whereas the Southern Chalk province links to the chalk of the Paris Basin and onwards to the Tethyan Realm (southern Europe, Mediterranean) (Mortimore *et. al.* 2001, 7). Geochemical analysis may reveal if these similarities are reflected in the flint that forms within these regions.

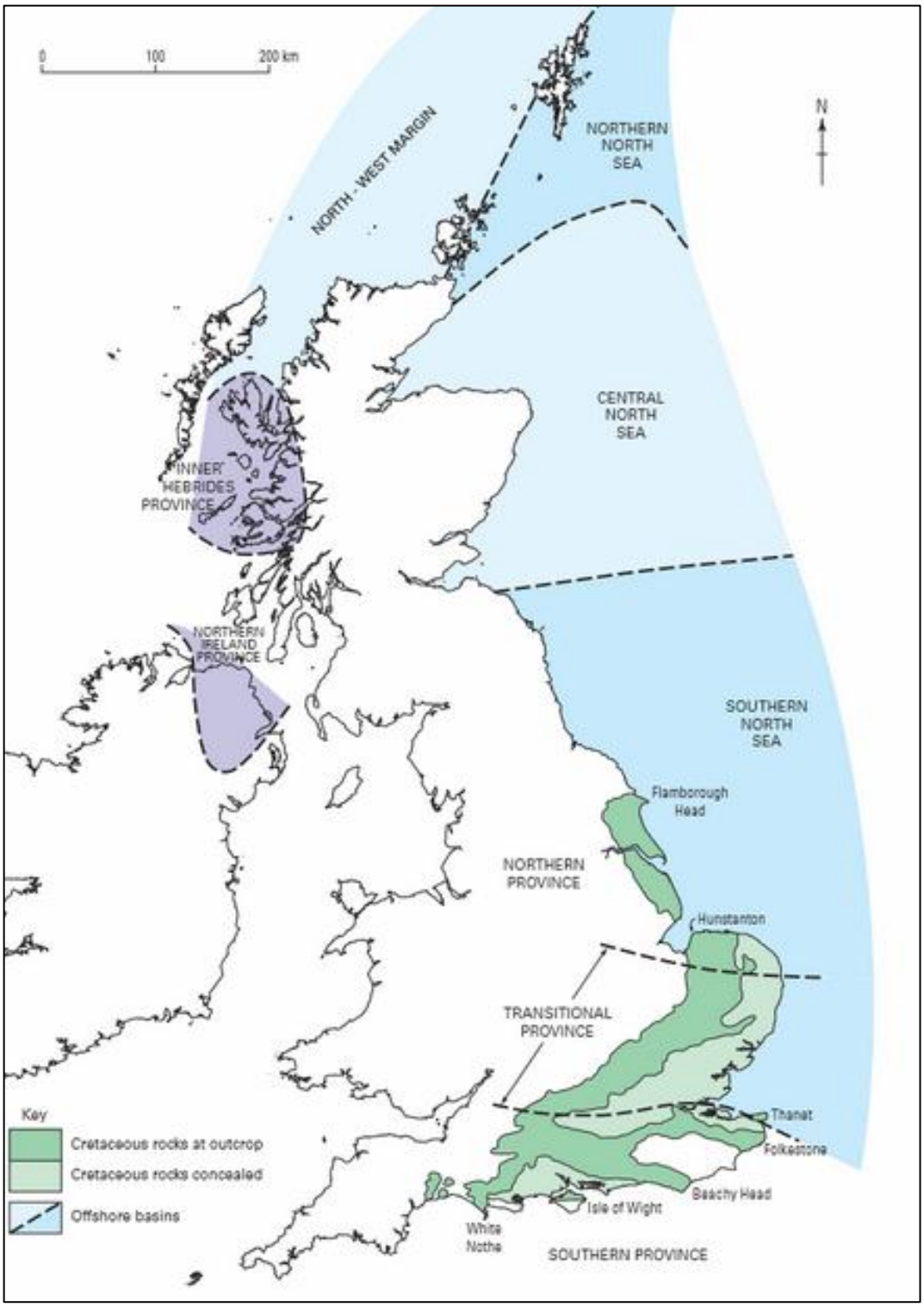


Figure 3.1 - Late Cretaceous chalk provinces in Britain and Ireland (Hopson 2005, 2)

As well as being divided into stages; Cretaceous chalk deposits are subdivided into a number of different formations through observation of distinct bedding features (Gale 2000, 357). The formations can be distinguished through biostratigraphy (fossil inclusions) and lithological markers such as flint or marl bands (Rawson 2006, 373). Bands of flint take the form of distinct layers of nodules or sheet-like tabular flint deposits. The relationship between the formations is illustrated below (Table 3.3).

<table>
<tr><td></td><td></td><td>Southern Province</td><td>Northern Province</td></tr>
<tr><td>Late Cretaceous Stage</td><td>Subgroup</td><td>Formation</td><td>Formation</td></tr>
<tr><td rowspan="2">Campanian</td><td rowspan="7">White Chalk</td><td>Portsdown (flint bands, less abundant than in Culver Fm.)</td><td>Rowe (abundant flint bands)</td></tr>
<tr><td>Culver (nodular flint)</td><td rowspan="2">Flamborough (flintless)</td></tr>
<tr><td>Newhaven (numerous flint bands)</td></tr>
<tr><td>Santonian</td><td>Seaford (nodular and tabular flint)</td><td>Burnham (tabular flint)</td></tr>
<tr><td>Coniacian</td><td>Lewes Nodular (nodular flint)</td><td rowspan="3">Welton (nodular flint)</td></tr>
<tr><td>Turonian</td><td>New Pit (flinty)</td></tr>
<tr><td>Cenomanian</td><td>Holywell Nodular (flintless in East Sussex, but flinty in Dorset)</td></tr>
<tr><td rowspan="2">Cenomanian</td><td rowspan="2">Grey Chalk</td><td>Zig Zag (flintless)</td><td rowspan="2">Ferriby (flintless)</td></tr>
<tr><td>West Melbury Marly (flintless)</td></tr>
</table>

Table 3.3 - Chalk lithostratigraphy in England (Hopson 2005, 6-49)

Despite once covering vast areas, substantial Cretaceous chalk deposits in Britain and Ireland are now only found in the northeast of Ireland and the south and southeast of England (Goudie 1993, 10). The remainder of the chalk deposits in Britain have been disturbed by uplift

at the end of the Cretaceous period which folded and disrupted the chalk, and erosion in the following Tertiary era (Toghill 2000, 152). In the north of Ireland, Cretaceous chalk deposits have been protected from erosion by Tertiary lavas of the Antrim Plateau (Wilson *et. al.* 2001, 331). These deposits are most visible along the northern and eastern coasts of County Antrim, although there are numerous smaller outcrops in the north of Ireland, notably in the Magherafelt area near Slieve Gallion (Herity & Eogan 1989, 103). There is also a small source of flint at Ballydeenlea, County Kerry, where a chalk deposit is located amidst substantially older geological formations (Davies 2011, 27). The chalk deposits in the north of Ireland are younger than their British counterparts; the deposition of chalk in Britain began during the Cenomanian stage of the Cretaceous (100 million years ago onwards) whereas the chalk in the north of Ireland has a base level dating to the Santonian stage of the Cretaceous (86 million years ago) (Wilson *et. al.* 2001, 345). Cretaceous deposits in Scotland have been severely disturbed, and largely buried, by geological processes during the Tertiary period, leaving only limited outcrops in Aberdeenshire and the Hebridean islands (Hopson 2005, 7). These deposits are of the same date as those located in the Northern, Southern, and Transitional Chalk provinces (Hopson 2005, 44).

The brilliant white colour of the chalk in Britain and Ireland is the result of arid conditions during the Late Cretaceous, when the chalk was being formed. Arid conditions on land resulted in a lack of sediment being washed into the sea by rivers, thus leaving the chalk free of impurities (Gale 2000, 356). The chalk in the north of Ireland is almost entirely organic, clay and silt make up between 1-2% of the chalk meaning that there was virtually no inflow from rivers when the chalk was forming (Wilson *et. al.* 2001, 345).

3.1.2 Flint

Chalcedony is the group name for cryptocrystalline varieties of silica, which are composed of minute quartz crystals with submicroscopic pores, including the minerals agate, chert, opal, jasper and flint (Allaby 2008, 98). Cryptocrystalline refers to the crystal structure of minerals which are too small to be observed under petrological microscopy, and are only partially visible under more powerful magnification (Allaby 2008, 144).

Flint is an opaque, granular form of chalcedony, which breaks with a conchoidal fracture (Bishop *et. al.* 1999, 133). It occurs in tabular layers or as bands of nodules within chalk (Rawson 2006, 388). Flint is composed of pure silica (SiO_2), with variable water content, and is chemically distinct from the calcium carbonate of the surrounding chalk (Toghill 2000, 145).

Chert and flint are terms that are sometimes used interchangeably in archaeological literature. This creates a great deal of confusion, particularly as there are several different working definitions: flint as a kind of chert (Cowell & Bowman 1985, 36; Gale 2000, 359); 'chert' used as another term for flint (Durst 2009); chert as geologically distinct from flint (Evans *et. al.* 2007); flint as a coloured variety of chert (Monroe & Wicander 2001, 167). However, the major division in terminology is geographic; North American archaeologists prefer 'chert', whereas British and Irish literature references 'flint'. In Britain, flint refers to the siliceous mineral that occurs in Cretaceous chalk deposits (Leudtke 1992, 5). This study will follow this usage, with flint referring to the siliceous mineral found in Cretaceous chalk deposits.

Flint is found in Cretaceous chalk deposits, in a variety of shapes and sizes. There are three main forms that flint occurs in: nodular, tabular/sheet, and paramoudra (Butler 2005, 17). Nodular flint bands are composed of irregularly-shaped lumps, of varying sizes (Figure 3.2). Tabular (or sheet) flint is characterised by thin, continuous seams of flint deposits (Figure 3.3).

Both nodular and tabular flint bands form horizontally in the chalk and can stretch over large distances (Rawson 2006, 388). Paramoudra flints are much rarer than nodular and tabular flints. Paramoudra flints vary in size (reaching >1m long in some cases), and are generally barrel-shaped, form vertically in the chalk and have a hole running through the centre (Mortimore 2010, 4). This hole is filled with unsilicified chalk and is surrounded by the flint itself, with can vary in thickness from a few millimetres to almost 1m (Bromley *et. al.* 1975, 8) (Figure 3.4).

The various forms of flint described above occur because of the different formation processes that occur within chalk deposits. The exact process through which flint is formed has long been a matter of debate amongst geologists (Butler 2005, 14). The basic process is that of silicification. Silicification is the gradual saturation of an organic structure with silica, where the carbonate elements of the structure are replaced by precipitation of silica cement (Flügel 2009, 643). With regards flint formation, the silica is of biogenic origin, originating from the mineral skeletons of radiolarians and diatoms (Monroe & Wicander 2001, 168).

Figure 3.2 - Bands of nodular flint at Ballintoy, Antrim

Figure 3.3 - Bands of tabular flint at the Arras Hill Chalk Pit, East Yorkshire (hammer is 320mm long) (Horne 2003)

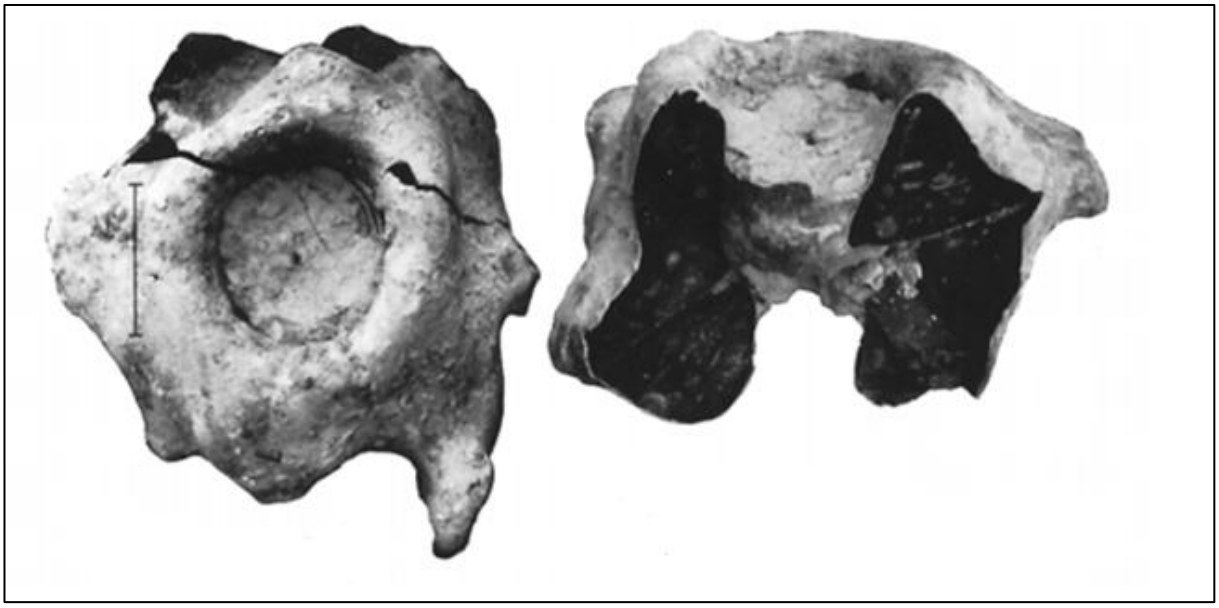


Figure 3.4 - Paramoudra flint, showing central hole (left) and surrounding flint (right). Scale bar is 10cm. (Bromley *et. al.* 1975, Plate 2)

There are several competing hypotheses regarding the exact conditions necessary for flint formation. The first of these is that flint formation occurs at the redox boundary. The redox boundary is a dividing line between oxic and anoxic conditions in sediment. Beneath the redox boundary, anaerobic bacteria produce hydrogen sulphide (H_2S), above this boundary; aerobic bacteria produce oxygen (O_2) (Gale 2000, 359). Oxidation of the hydrogen sulphide occurs at the redox boundary, lowering the local pH and causing silica to precipitate out of the solution, creating areas of siliceous deposits, which then harden into flint (Carozzi 1993, 160). A number of authors suggest that flint forms through precipitation of biogenic silica out of solution, nucleating around sites of concentrated organic matter such as burrows and fossils (many flints show evidence of these features) (Bromley & Ekdale 1984, 298; Toghill 2000, 145; Rawson 2006, 388; Allaby 2008, 219).

The process through which a solution of biogenic silica hardens into flint is also a matter of debate amongst geologists. The general process is considered to be the gradual replacement of the calcium carbonate of the chalk by silica, incorporating the non-carbonate materials (clay minerals, quartz, and heavy minerals) that are, in effect, contamination (Sieveking *et. al.* 1970, 252). It is this preservation of the non-carbonate material within flint that provides the theoretical framework that underpins geochemical provenancing (Bush & Sieveking 1986, 134).

Hancock (1975) posits that the process of flint formation is best understood as the transformation of opal-A to opal-CT. Opal-A is the term for the amorphous, hydrous form of silica that is precipitated by decaying marine organisms (Pettijohn *et. al.* 1987, 439). This becomes opal-CT, an intermediary stage in the transformation of opal-A to quartz (Davidovits 1986, 516).

Nodular flint forms preferentially in areas with concentrated organic matter, particularly burrows of small crustaceans (Allaby 2008, 118). This explains the irregular, convuluted shapes of flint nodule formations (Figure 3.5); however it is acknowledged that not all flints form in this manner (Bromley & Ekdale 1986, 74). Tabular flint forms following the same silicification process as nodular flint, percolation of silica-rich fluid through sedimentary layers (Wilson *et. al.* 2001, 346). However, the main difference is that tabular flint is formed in continuous sheets as opposed to discrete, scattered nodules. Paramoudra flints differ from both nodular and tabular flint as they form vertically within the chalk. They form around burrows, but not within the burrow, as this is represented by a cylinder of chalk running through the centre of the paramoudra (Figure 3.4) (Rawson 2006, 388). Paramoudra are thought to form around a locally reducing environment (the burrow), with silicification occuring some distance away at the boundary with oxidising conditions (Clayton 1986, 50).

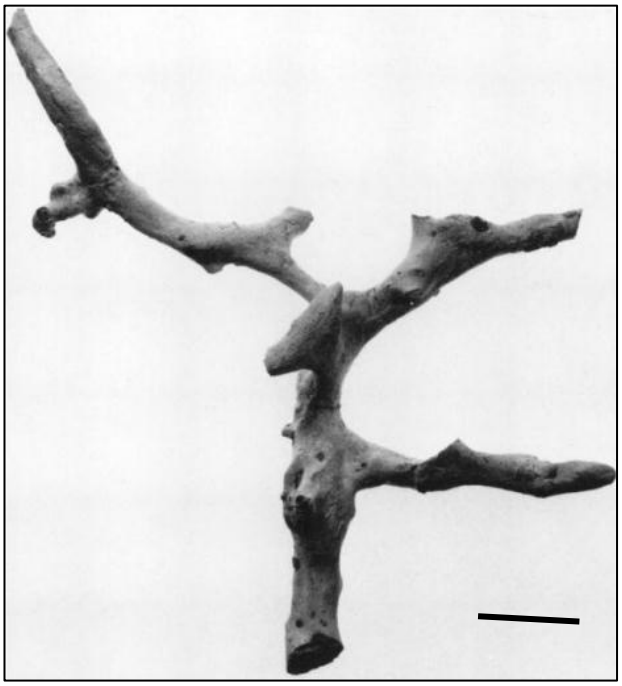


Figure 3.5 - Silicified *Thalassinoides paradoxicus* burrow (scale bar 5cm) (Bromley & Ekdale 1984, 301)

3.2 Sources of flint

The processes above describe the formation of flint within Cretaceous chalk deposits. Where flint is found *in situ* in chalk, it is referred to as a primary source. The primary sources of flint are shown in Figure 3.1, in areas of Cretaceous chalk outcrops. Secondary sources are those that have been eroded out of the parent chalk through glaciation, frost and wave action, as well as buried river gravels (Butler 2005, 17). In terms of provenancing, primary deposits of flint should be useful for obtaining a signature of a specific area. Secondary deposits, however, have been moved from the parent rock and will not provide a signature of the area in which they are found, but a signature of where the flint originated, which may be from offshore chalk deposits (Cowell & Bowman 1985, 36; Dawson & Dawson 2000, 96).

Secondary sources of flint in Britain and Ireland vary widely, and can be found across huge swathes of the landscape. Important secondary sources of flint include, but are not limited to: flint from glacial deposits in the Yorkshire and Lincolnshire Wolds in the form of small pebbles (Mithen 2007, 51); redeposited pebbles on the Buchan Ridge, Aberdeenshire (Warren 2006, 35); and extensive clay-with-flints deposits in the South Downs (Butler 2005, 18). Clay-with-flints deposits are the disturbed and disorganised remnants of what was once an intact Cretaceous chalk deposit. They contain clay and unworn flint, and are formed through the dissolution of chalk deposits, as well as the folding and faulting of the deposits in the Miocene (Gallois 2009, 153).

3.3 Qualities of flint

Flint, when found in primary deposits, ranges in colour from grey to black (Butler 2005, 20).1111 However as soon as flint is exposed to the atmosphere or buried, it can change colour through weathering or by absorption of minerals from the groundwater. The chalky, outer

surface of primary sources of flint is called the cortex and represents the boundary between the siliceous flint and the parent chalk (Figure 3.6).

Figure 3.6 - White, chalky cortex (arrowed) on the exterior surface of dark grey flint (photo: author)

In flint that has been recently removed from the chalk, this cortex remains chalky and soft. Secondary sources of flint lose this chalky cortex and instead have a 'chattered', rougher exterior surface from water-rolling, and the effects of weathering (Berridge & Roberts 1986, 15). Flint can also contain pieces of chalk within the nodule, and frequently contain fossil inclusions (Figure 3.7).

Figure 3.7 - Flint with belemnite fossil inclusion (arrowed) (photo: author)

3.3.1 Patination

Patination refers to changes on the exterior surface of flint. Like 'chert', the application of 'patination' varies widely and causes considerable confusion. Patina has been variously defined/explained as; long-term oxidation of the exterior surface (Bakels 2009, 18); short-term oxidation of the exterior surface (Butler 2005, 20); leaching of minerals from the surrounding soil environment (Cowell & Bowman 1985, 36-7); the result of weathering (Gibbard 1985, 143); leaching of silica from the flint (Graetsch & Grünberg 2012, 23); and burial in alkaline environments (Keeley 1980, 29).

These aetiologies differ greatly, and have serious repercussions on attempts to identify geochemical signatures. Flint patina can vary greatly within both primary (Figure 3.8) and secondary sources of flint. X-ray fluorescence is a method used for geochemical provenancing, and has been successfully applied to flint sources (Högberg *et. al.* 2012). For this kind of analysis, the exterior surface of the flint is removed to prevent contamination from the patina (Gauthier *et. al.* 2012, 2450).

Figure 3.8 - Differential patination in a primary flint source (White Rocks, Antrim)

For this study, patina will refer to the exterior surface of flint, distinct from cortex, which differs in colour from unpatinated flint. Until the influence of patina on geochemical analysis has been determined, it will be removed from the flint prior to analysis to reduce contamination.

3.4 Scientific analyses of lithic material

The scientific study of stone found in archaeological contexts has been underway for almost a century. As new approaches and techniques become available, they are incorporated into investigations, most frequently with regards provenancing and chemical characterisation.

Commercial ICP-MS analysis was initially applied to biological material, before being used to provenance ceramics, metal, soil and obsidian (Pollard *et. al.* 2007, 208).

3.4.1 Stone

The beginning of scientific analysis of lithic material arguably began with H. H. Thomas, who sourced the Stonehenge bluestones to the Mynydd Preseli region of Wales, using petrographic means (Thomas 1923). Petrography involves the creation of thin slices of stone, obtained from the implement or raw material. These slices are sawn or drilled from the stone, and are ground or polished to a thickness of 30 µm. The slices are examined under polarising microscope, which uses different polarisations of light to reveal distinguishing characteristics of constituent minerals (Rapp & Hill 1998, 239). The constituent minerals of the implement and the raw material can then be compared to attempt to locate a likely source. Thomas' analyses involved side-by-side examination of thin slices of stone from the Stonehenge bluestones, and samples taken from the raw material source in Wales. This analysis was accepted until recently, when re-examination of the bluestones using instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) proved that they were from the Pont Saeson region of Wales (Bevin *et. al.* 2012).

The widespread use of stone axes began during the Neolithic period. These axes are manufactured from a variety of raw materials, the geological sources of which can be found across the British and Irish mainland, as well as smaller islands. There have been several major publications dealing with implement petrology in Britain and Ireland; chief amongst these are the Stone Axe Studies I and II (Clough & Cummins 1979; 1988) and Stone Axe Studies III (Davis & Edmonds 2011). These monographs include attempts to identify raw material sources and geochemical characterisation of implements from across Britain and Ireland, operating under

the assumption that the widespread distribution of axes manufactured from various lithologies was due to anthropogenic means. However, there is considerable debate surrounding the lengths to which prehistoric people went to obtain raw material for axe manufacture, with some archaeologists suggesting that stone moved through glaciation (glacial erratics) provided most, if not all, the raw material required for axe-making (Briggs 1976; 1977). There is no doubt that glaciation distributes large amounts of material across huge distances, however the area of distribution is limited to the extent and direction of the glacier itself (Monroe *et. al.* 2007, 547).

One of the most contested examples of stone transportation is the method by which the bluestones used in the construction of Stonehenge arrived in Wiltshire from the Preseli hills, south Wales. This theory draws on the fact that Irish Sea ice over-rode the south of Wales and travelled in a south-easterly direction, towards Salisbury Plain (Robinson 2001, 13). This would have allowed for the glacier to remove stone from the source and transport it towards Wiltshire. It is now widely accepted that the bluestones arrived in Wiltshire as the result of human transportation (Thomas 1999, 178; Parker-Pearson 1999, 89).

Glaciers cannot be used to explain the transportation of the Stonehenge bluestones; however the use and distribution of quartz dolerite implements may show more of a correlation with glacial movement in the past. Sources of quartz dolerite are limited in Britain, restricted to the north of England and Scotland, and were utilised in the past to manufacture Group XVIII and XXVIII axes (Clough 1988, 8-9). Williams-Thorpe *et. al.* (1999) used X-ray fluorescence to match quartz dolerite pebbles contained within glacial till to their geological source, demonstrating the movement of a specific lithology due to glaciation. The quartz dolerite was moved from the source in northern England to eastern England, and there is a marked correlation between the distribution of quartz dolerite erratics and implements manufactured from this material

(Williams-Thorpe *et. al.* 1999, 209). However, Williams-Thorpe *et. al.* (1999, 237) acknowledge that there are a number of implements made of quartz dolerite that fall outside the range of glacial distribution.

It is not unreasonable to suggest that a proportion of stone axes in the past were manufactured from glacial erratics (Bradley & Edmonds 2005, 38). However, the suggestion that glacial erratics were (almost) exclusively used for raw material does not take into account the huge amount of archaeological evidence at quarries and mines that testifies to the importance of these sites. The extraction sites for porcellanite, Langdale tuff and Cornish gabbro are characterised by tons of waste flakes and debris, demonstrating the long-term, intensive exploitation of these areas (Edmonds 2005, 49). Glaciation also cannot account for the movement of certain types of raw material; the north and easterly distribution of Cornish greenstones is due solely to trade and exchange as glaciers did not travel from the southwest to the east or north (Clough 1988, 5). In the southeast of England, beyond the reaches of even the most extreme estimates of ice cover, the presence of stone axes and other implements made on non-local material bears witness to the existence of trade networks during the Neolithic period (Woodcock *et. al.* 1988, 23).

Petrographic determination of raw material source can be achieved relatively easily, depending on the lithology; however it is impossible to determine petrologically or geochemically whether raw material was transported via glaciation or through human means (Cummins & Harding 1988, 80). Although opportunistic exploitation of glacial erratics undoubtedly occurred in some areas, the vast majority of stone implements were manufactured from specifically-sourced lithologies which were traded widely due to their inherent exoticism, and symbolic significance (Edmonds 2005, 53). As glacial erratics are of limited significance for stone implement manufacture, petrological studies are immensely

valuable for providing a greater understanding of the exploitation, trade and use of stone sources in prehistory.

Stone Axe Studies II (Clough & Cummins 1988) details the petrological methodology employed for provenancing stone artefacts; microscopic examination of samples taken from implements. Samples were obtained from stone axes using the methodology described below (Fenton & Travis 1989, 12-3):

- Water-cooled, diamond core-drill penetrates artefact at a suitable point (i.e. damaged area);
- core broken off at base by gentle leverage;
- top 2mm of the core, bearing original surface, sawn off for use in restoration;
- remainder of core is sawn longitudinally, the cut made slightly off-centre to obtain the largest possible section;
- The larger piece is ground flat, mounted on a glass slide, and the excess is sawn off and polished to produce a thin section.

The benefit of this approach is that multiple samples can be obtained from the same core, preventing the need for re-sampling and further destruction of the artefact. Using this technique, implement petrologists have determined 34 main stone axe groups in Britain, Ireland, and France, sourced the sites of raw material procurement, and are able to reconstruct trade networks. The most numerous lithologies encountered are Langdale Tuff (Figure 3.9), porcellanite, gabbro and augite granophyre; these groups have extensive distribution networks across Britain and Ireland, despite restricted availability of raw material (Clough 1988, 7-10). Thin sections taken from implements are compared to thin sections taken from the potential source material. At Langdale, samples were obtained from flaking sites and areas where the raw material appears similar to Langdale axes; these were then prepared as

thin sections for comparison to the implement material (Houlder 1979, 87-8). This approach was also utilised for the analysis of jadeite axes from northern Italy. Thousands of raw material samples were obtained from the source areas in the Alps and prepared as thin sections; these were compared to thin sections taken from implements to determine if the constituent minerals correlate (Sheridan 2007, 25).

Implement petrology has also been used to source axes of exotic lithologies found in Britain and Ireland. The most obvious imports are axes made of jadeite (3.10), the nearest source of which is the Alpine region of northern Italy (O'Haplin & Newman 2006, 3).

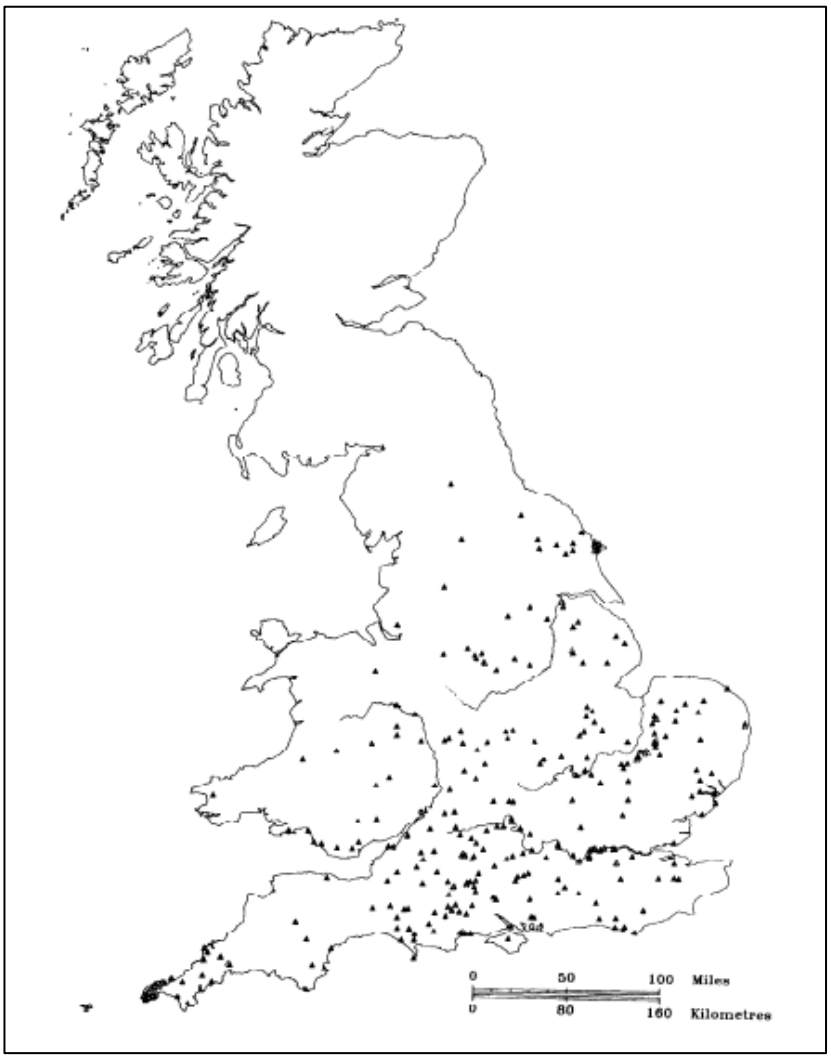


Figure 3.9 - Distribution map of Cornish Gabbro axes (Group I) in Britain (Clough & Cummins 1988, 266)

Figure 3.10 – Jadeite axe in the National Museum of Scotland (Stone Project 2013)

Jadeite axes were initially analysed using an electron microprobe, a non-destructive method which directs an electron beam at the material, releasing x-rays at the wavelength characteristic of a particular element. This technique was used by Woolley *et. al.*, and is preferable to thin-sectioning rare or particularly fine artefacts (Woolley *et. al.* 1979, 95). The pan-European *Project JADE* used reflectance spectroradiometry in conjunction with X-ray diffraction and electron microprobe analysis to achieve in excess of 70% accuracy in sourcing jadeite axes to one of two northern Italian Alpine sources; Monte Viso and Monte Beigua (Sheridan 2007, 25-6).

There are other lithologies in Britain that have been examined in terms of distribution networks in relation to a restricted source. One such material is pitchstone, a glassy volcanic rock, distinguished from obsidian by its higher water content (Thorpe & Thorpe 1984, 1). Pitchstone is found on the island of Arran, Western Scotland, and in Northern Ireland. The sourcing of pitchstone artefacts is largely based on the assumption that all raw material was

sourced from Arran, as it is only the material from Arran that is suitable for tool making (Ballin 2011, 8). This assumption is borne out by research that has sourced pitchstone artefacts found in Antrim to the pitchstone outcrop in the Corriegills area of Arran, despite locally-available pitchstone in Antrim (Preston *et. al.* 2002, 219). Bloodstone is a form of chalcedony, restricted to several small outcrops in on the west coast of Scotland. The island of Rhum in the Inner Hebrides provides the only source containing enough material to be useful in prehistory (Wickham-Jones & Pollock 1985, 21). As Rhum contains the largest source, and perhaps the most widely-known, artefacts made of bloodstone are frequently attributed to this source despite an absence of geochemical evidence to corroborate this (Rainbird 2007, 151).

Petrological approaches are suitable for many lithologies, as they contain large crystals that can be seen under petrographic microscopes. Flint, however, has a cryptocrystalline structure which debars the use of thin sections or petrographic microscopy.

3.4.2 Obsidian

Obsidian is a silicic glass formed when extruded lava cools quickly, with minimal crystal growth (Figure 3.11) (Shackley 2005, 10-11). Obsidian does not occur naturally in Britain or Ireland, although it has been the subject of a number studies investigating geochemical provenancing, with excellent results. Initial studies of obsidian used instrumental neutron activation analysis (INAA), a method that involves the irradiation of a small sample taken from the artefact - this irradiation is achieved through use of a nuclear reactor (Pollard *et. al.* 2007, 129). Using INAA, Thorpe *et. al.* (1984, 183) analysed 270 archaeological obsidian artefacts and determined provenance to three Carpathian obsidian sources. INAA has been largely replaced by ICP-MS, as the latter can detect a wider range of trace elements at lower concentrations (Durst 2009, 24). The basic methodology for ICP-MS analysis is outlined below:

- sample obtained from artefact/source and ground into powder
- powder dissolved in acid or melted in a lithium metaborate flux
- resulting solution is mixed with nitric acid and run through a mass spectrometer

ICP-MS, although a time-consuming and destructive technique, provides accurate results and has been successfully used to characterise obsidian sources used for tool making at Çatalhöyük, Turkey, where a long-term provenancing study has matched 135 obsidian artefacts to three Cappadocian sources; Göllü Dağ-east, Nenezi Dağ and Acigöl West (Carter *et. al.* 2006, 893).

Non-destructive analyses have proven spectacularly successful, particularly LA-ICP-MS and XRF (Negash *et. al.* 2006; Phillips & Speakman 2009). LA-ICP-MS was used to characterise obsidian flows in Anatolia and the Aegean, and archaeological obsidian tools were matched to sources (Gratuze 1999). Portable XRF (pXRF) has been used to source artefacts in the field, reducing the amount of sample preparation and allowing archaeologists to obtain results during the excavation (Milić 2013, 285).

The relative ease with which obsidian can be sourced is due to a number of factors, including its relatively restricted occurrence, chemical homogeneity and the ability to use a number of methods to investigate provenance (Williams-Thorpe 1995, 217). The chemical composition of obsidian can be characterised with relative ease due to the homogeneity of the material itself. Each source shows very little internal chemical variation, although each source differs from another; even if they are geographically close (Godfrey-Smith *et. al.* 1993, 385).

The long research history of obsidian sourcing (provenancing first described in Brothwell & Higgs 1963) has led to a proliferation of studies; the method proven, advances in instrumentation are now providing almost instantaneous results. A recent programme of pXRF

analysis in Armenia used pXRF in the field, as opposed to during post-excavation analysis, and achieved results in approximately 10 seconds (Frahm *et. al.* 2014). The cumulative effect of these studies has led to greater understanding of the distribution of artefacts made from a particular obsidian source, illustrating by proxy the trade networks that existed in eastern Europe and Anatolia in prehistory (Figure 3.12).

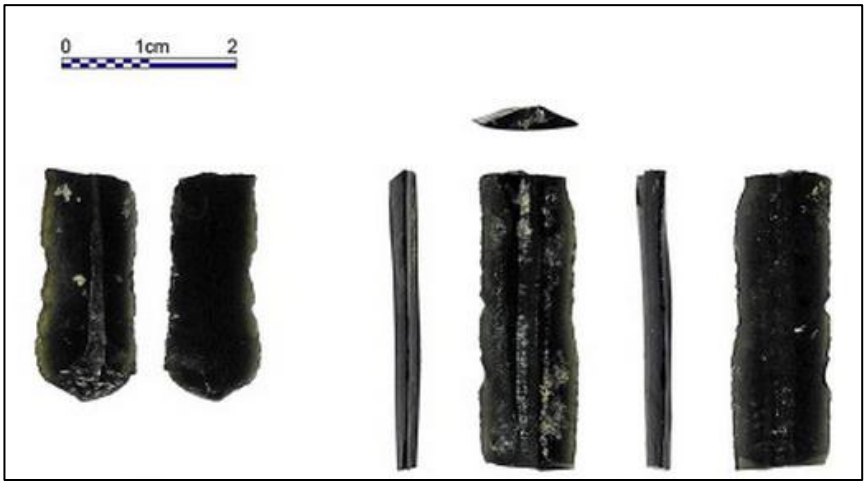


Figure 3.11 - Obsidian artefacts from Tell Mozan, Syria (Frahm and Feinberg 2013, 1869)

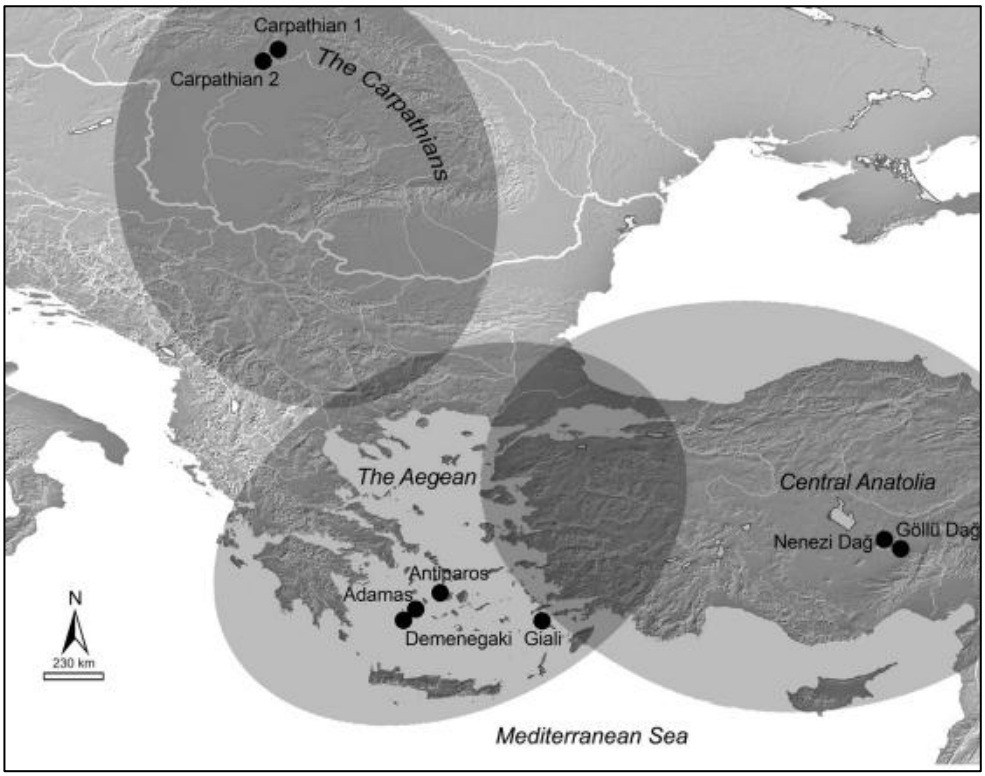


Figure 3.12 - Major obsidian sources and artefact distribution areas (Milić 2013, 286)

3.4.3 Flint

There are numerous studies focussing on the diagenesis and distribution of flint that appear in geological literature (Reid 1971; Madsen & Stemmerik 2010; Lindgreen *et. al.* 2011), however geochemical provenancing of flint has not enjoyed the same attention as obsidian sourcing or stone implement petrology. This may be due to the comparative difficulty in characterising flint sources compared to obsidian. Flint sources are chemically heterogeneous, and cannot be characterised with the same precision as obsidian sources. Flint cannot be provenanced based on visual inspection, and petrological analysis cannot be applied to flint, as thin sections of flint do not reveal distinctive mineral structures that can be matched to raw material sources (Tingle 1998, 89).

One of the first attempts to chemically distinguish between flint sources in Britain was conducted through the use of atomic emission spectroscopy (AES) and atomic absorption spectroscopy (AAS) (Sieveking *et. al.* 1972). These methods analyse the composition of a sample by detecting the light emitted from or absorbed by elements as they interact with a flame or plasma; the wavelength of the light is detected by a spectrometer and chemical characterisation can be obtained. Samples were obtained from known prehistoric flint mines in Britain (Grime's Graves, Beer, Easton Down, Blackpatch, Cissbury, Clanfield and Peppard) in order to determine the variation within and between these areas. Sieveking *et. al.* (1972, 164) found that it was possible to distinguish between flint from these mines, and that there were a number of elements that proved useful in discriminating between different source regions; Aluminium (Al), Magnesium (Mg), Iron (Fe), Potassium (K), Sodium (Na), Lithium (Li) and Phosphorus (P) - these are attributed to the clay minerals, phosphates and organic matter that would have been present in the sea during the formation of the chalk.

Where Sieveking *et. al.* (1972) focussed on distinguishing different raw material sources, other studies have attempted to trace this raw material across the landscape. Griffiths & Woodman (1987) used electron spin resonance analysis (ESR) to uncover the raw material source of Late Mesolithic flint tools found in the Bann Valley, in the north of Ireland, which are found a considerable distance from large sources of flint. Electron spin resonance is an approach whereby the electromagnetic radiation of unpaired electrons is measured. This radiation is at a specific frequency which allows the elements to be identified (Ikeya 1993, 24). Griffiths & Woodman (1987, 250) sampled flint from three sources (Carnlough beach, Slieve Gallion, Carmaen (*sic)*) and two excavated assemblages (Bay Farm 1 and Newferry) in an attempt to trace artefacts to raw material sources. The sites with the most number of samples, Slieve Gallion and Carnlough beach, present almost mutually exclusive ESR values, demonstrating

both that flint sources in the north of Ireland are chemically distinct, and that multiple samples from any one source are required for chemical differentiation (Griffiths & Woodman 1987, 251). In addition, artefacts from Newferry corresponded most closely with the flint source at Carnlough beach, indicating that the raw material was being traded inland from coastal procurement sites.

A later approach to flint provenancing in Britain was Rockman's (2003) use of LA-ICP-MS and acid digestion ICP-MS to characterise British and French flint sources and provenance Upper Palaeolithic artefacts to raw material sources. This study proved that geographic regions containing sources of flint were sufficiently geochemically distinct to permit attempts at provenancing. Rockman identified three major source regions that can be distinguished by LA-ICP-MS: south-western England chalk flint, northeastern England chalk flint, and southwestern clay-with-flints (Rockman 2003, 343-4). This study also revealed a number of elements that were useful as discriminants between different source areas of British flint, with the concentration of Rubidium as an important tool for distinguishing between source regions (Rockman 2003, 348);

- Rubidium (Rb) separates the South Downs from Grime's Graves
- Praseodymium (Pr) separates Beer clay-with-flints from the northern flint
- Uranium (U) separates Pewsey/Beer flint and Beer clay-with-flints from Withernsea cobbles
- Rubidium, Uranium and Lanthanum (La) separate Beer clay-with-flints from Withernsea cobbles

It was anticipated that acid digestion ICP-MS would provide more accurate results than LA-ICP-MS as it can detect a greater range of elements, and at lower concentrations. However, Rockman's analysis established that LA-ICP-MS and acid digestion ICP-MS may not provide

substantially different results, as flint from Pewsey and Beer analysed using both methods show very little separation from each other (Rockman 2003, 347). However, acid digestion ICP-MS provides substantially more precise measurements and may potentially provide much greater geographic resolution (Rockman 2003, 333). The artefactual analysis demonstrated that the flint sources in the southwest of England (Pewsey and Beer) were of considerable importance during the Upper Palaeolithic in Britain. 12 flint tools from Robin Hood's Cave, Derbyshire, revealed chemical signatures that correlated most closely with Pewsey/Beer source regions; these artefacts were chosen from multiple stratigraphical layers demonstrating the length of use of this source region for raw material (Rockman 2003, 359).

Building on this research, Pettitt *et. al.* (2012) used LA-ICP-MS to obtain geochemical signatures of major areas of British bedrock flint, as well as secondary sources. The chemical signatures of these regions were compared to 28 British Upper Palaeolithic flint tools in order to infer group mobility and raw material movement during this period (Pettitt *et. al.* 2012, 275). This study found that raw material was being transported huge distances across the landscape; four flint tools from Bradgate Park, Leicestershire, matched closely with East Anglian flint sources, implying a transport distance of around 100km (Pettitt *et. al.* 2012, 282). Each site sampled in this research provided evidence for the use of more than one raw material source, and the authors urge caution in interpreting provenancing data as the lithic remains on any given site are likely to be a fraction of what may have been present, leading to an underestimation of the number, direction and distance of sources utilised in the past (Pettitt *et. al.* 2012, 282). This study found that the relevant discriminant elements for distinguishing between flint sources at major geographic scales - Wolds, East Anglia, North Downs and South Downs - were Aluminium, Potassium, Rubidium, Zirconium (Zr), Niobium (Nb) and Barium (Paul Pettitt *pers. comm.*).

Acid digestion ICP-MS can detect a wider range of elements when compared to LA-ICP-MS, including rare earth elements (REE). Rare earth elements are not so called because they are scarce, but rather because they are dispersed and do not occur in concentrated quantities in rare earth minerals (Miyawaki & Nakai 1996, 21). In a 2011 study, Olofsson & Rodushkin attempted to discover the source of flint used for tool making in Sweden. As flint does not occur naturally in Sweden, all such material must be the result of trade or direct procurement. Six samples were obtained from archaeological flint tools, along with a total of 19 samples from reference material from Denmark and Russia (Olofsson & Rodushkin 2011, 1147). These samples were ground into powder and analysed using acid digestion ICP-MS. Olofsson and Rodushkin discovered that Lead isotopes ($^{208}Pb/^{206}Pb$) varied in a systematic way and can be used as a discriminant element between South Scandinavian Cretaceous flint and Russian Carboniferous flint (Olofsson & Rodushkin 2011, 1154). The ratio of REE Cerium (Ce) and Lanthanum also provides clear differentiation between eastern and western Danish flint sources (Olofsson & Rodushkin 2011, 1159). The ratios of discriminant REE are interpreted as the result of different depositional environments in which the flint has formed (Olofsson & Rodushkin 2011, 1160). The sources of flint in eastern Denmark show little chemical variation when compared to the sources in the west; however analysis of the REE, as well as lead isotopes, can overcome this homogeneity and facilitate differentiation (Olofsson & Rodushkin 2011, 1165).

Research into southern Scandinavian sources of flint continued with XRF analysis conducted by Högberg *et. al.* (2011). This study analysed flint from 25 different localities in southern Scandinavia in an effort to characterise source geochemistry. Högberg *et. al.* selected nine elements as discriminants; aluminium, sulphur (S), chlorine (Cl), titanium (Ti), manganese (Mn) potassium, silica (Si), calcium (Ca) and iron (Högberg *et. al.* 2011, 228). In addition to

characterising source geochemistry, Högberg *et. al.* also tested the patinated and unpatinated surfaces of the samples in order to determine the influence of patination on geochemical provenancing. The results of this show that patinated surfaces on flint show a depletion of silica and elevated levels of iron, chlorine and titanium, and that patina can negatively influence chemical analyses (Högberg *et. al.* 2011, 230). This study also re-sampled flint analysed in a pilot study conducted by Hughes *et. al.* (2010), which analysed 50 samples from southern Scandinavian flint using XRF and found that they formed three chemically distinct groups; Hanaskog, Östra Torp, and Stevns Klint (Högberg *et. al.* 2011, 230).

3.5 Conclusion

The formation of flint is debated, but likely to be the result of silicification of organic material, under a variety of circumstances. Flint is generally thought to be a relatively homogeneous material; however the successes of recent provenancing studies have shown that it is possible to achieve some degree of specificity in terms of raw material sources. Högberg *et. al.* identify a number of problems with reliance on macroscopic methods of identification, chief amongst which is that they found no correlation between the flint's visual appearance, source location, parent chalk or chemical composition (Högberg *et. al.* 2011, 234).

Geochemical analysis of flint is likely to be complicated by patination, weathering and redeposition; however these problems are not insurmountable. Analysis of flint samples for geochemical provenancing can circumvent any potential problems from a weathered or patinated surface by removing them prior to subsampling. However as the effects of these surfaces on provenancing are not fully understood, comparative analysis of patinated and unpatinated surfaces will be useful in determining their geochemical variability.

Acid digestion ICP-MS provides the best option for obtaining a detailed geochemical signature of flint, as it relies on a much larger set of elements, at smaller concentrations, with the potential for greater precision compared to XRF and LA-ICP-MS. However, this is a destructive method which will cause difficulties if applied to archaeological artefacts. Non-destructive, accurate analysis is the gold standard of provenancing, particularly in attempts to match artefacts to sources of raw material. There are various analytical methodologies that have been applied to provenancing stone and flint from archaeological contexts, each of which have advantages and disadvantages. The approaches taken throughout archaeometrical studies are outlined in the following chapter.

4.0 GEOCHEMICAL ANALYSIS OF FLINT

This chapter will discuss the potential for determining the geochemical signature of sources of flint within Britain and Ireland using inductively coupled plasma mass spectrometry (ICP-MS) and portable X-ray fluorescence (pXRF). Flint has been chosen for this study due to its extensive use throughout the study period, despite its relatively restricted geological occurrence. Obtaining source-specific signatures will allow for the reconstruction of networks of trade and exchange, providing valuable insights into the movement of raw materials and by

proxy, people, during the Mesolithic, Neolithic and Bronze Age. This section will outline ICP-MS and pXRF analysis procedures and justify the use of these methods for this study.

Archaeological methods of determining raw material are poorly developed; previous studies have used various macroscopic features to assess the source of worked flint; colour (Suddaby & Ballin 2010, 42), proximity of the source to the site (Costa *et. al.* 2001, 1; Driscoll 2010, 28) or cortical texture (Conneller & Schadla-Hall 2003, 88). These attributes have limited use in determining provenance, and have greater degrees of error than geochemical methods (Andrefsky 2005, 42). Geochemical analyses of stone rely on accurately determining the elemental composition of lithic artefacts and source areas, providing the proportion of different elements in the sample. Ideally, the proportions of elements will vary between sources, allowing artefacts to be traced to discrete geochemical outcrops.

4.1 Inductively Coupled Plasma-Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) combines a high-temperature plasma and a mass spectrometer, allowing for the detection of trace elements within a given sample (Wolf 2005). ICP-MS is highly sensitive and can detect a wide range of elements at low concentrations, as low as a few parts per billion (Durst 2009, 24). However, there are some restrictions on the elements that can be detected using ICP-MS. Figure 4.1 identifies the elements that can (and cannot) be determined, as well as the approximate detection limit ranges.

Figure 4.1 - Elements determined by ICP-MS and approximate detection limits (Wolf 2005)

4.1.1 Sample Preparation

There are two sampling methodologies that ICP-MS can use to provide geochemical signatures necessary for this study. Both of these methods provide the requisite sensitivity, however they differ significantly in terms of sample preparation and suitability for use on archaeological artefacts - laser ablation (LA-) ICP-MS and acid digestion ICP-MS. Sample preparation is key in ICP-MS analysis, as the sensitivity of the method means that any contamination will interfere with the results.

LA ICP-MS is a quasi-non-destructive approach (figure 4.2) used to detect proportions of elements in a given sample. LA ICP-MS cannot be classified as a non-destructive method as a small amount of the sampled material is destroyed (between 5 and 400µm (Pollard *et. al.* 2007, 198). Laser ablation analyses samples in a solid state with minimal preparation, avoiding the difficulties inherent in generating a solution from inorganic solids. There are restrictions however, as the sample must be small enough to fit into the sample chamber. The sample must also be microscopically flat, requiring the polishing of a resin-imbedded sample (Pollard *et. al.* 2007, 197). An ultraviolet laser is used to ablate a small area of the sample, the products of which are carried to the plasma torch in a stream of argon (Speakman 2012).

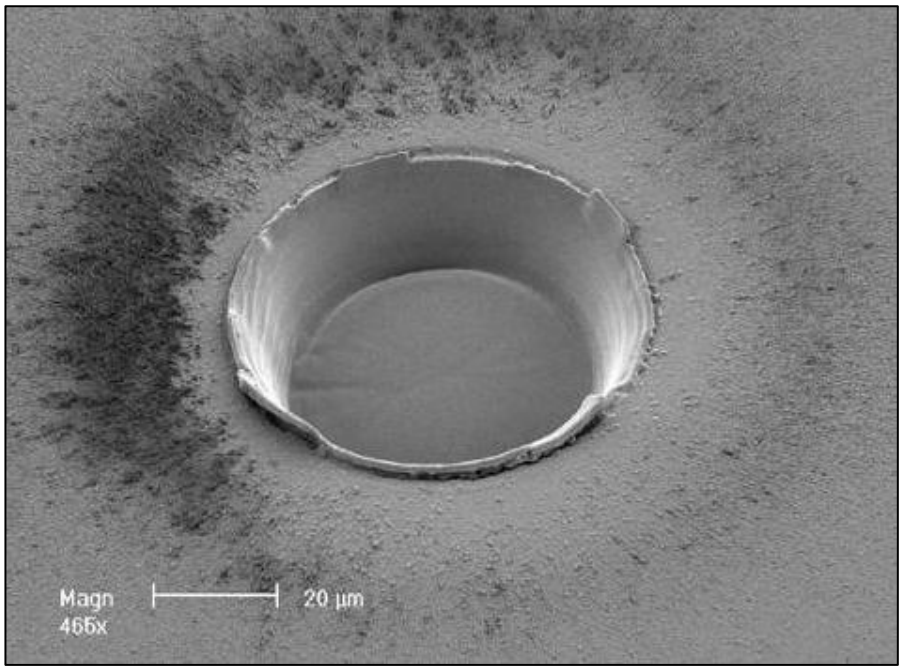


Figure 4.2 - Laser ablation scar on igneous rock (Stamper 2013)

LA ICP-MS is susceptible to matrix effects; this is where components of the sample influence the measurement of the analyte, meaning that ablation products may not be truly representative of the sample.

An alternative method for preparing samples involves digesting a small amount (~1-2g) of the sample in acid, creating a solution that can be introduced to the plasma torch. The type of acid used depends on the sample matrix - flint, with its high silica content, would ideally be dissolved with hydrofluoric acid (Dean 2005, 22-3). However, due to the health and safety concerns surrounding the use of hydrofluoric acid, it was not used in this study, nitric acid was used instead. Acid is then added to the sample and the solution is heated. This commonly occurs in open glass vessels on a hot plate or within a microwave (in either closed or open vessels) (Dean 2005, 24). The basic procedure for acid digestion is as follows:

- Solid sample reduced to appropriate size (i.e. flint reduced to powder)

- Sample weighed out into vessel
- Acid added to sample
- Solution heated on hot plate or in microwave

The fully-digested solution is then measured out into small plastic test tubes and placed into the auto-sampler prior to ICP-MS analysis.

Samples can also be decomposed using alkali fusions, including (but not limited to) lithium metaborate, lithium tetraborate or sodium carbonate; this approach is particularly apposite for geological or metallurgical samples (Jarvis *et. al.* 2003, 196). The sample is fused in a crucible at 900-1050°C in a muffle furnace, and the melts are then dissolved in nitric acid (Jarvis *et. al.* 2003, 197).

4.1.2 Generation of plasma

Below is a schematic representation of ICP-MS analysis, from introduction of the sample to detection of ions (Figure 4.3). Plasma is the co-existence of positive ions, electrons and a neutral species of an inert gas in a confined space (Dean 2005, 57). The function of the plasma is to form positive ions from the sample aerosol (Agilent Technologies 2005, 13). A coupling coil is used to apply radio frequency to a heated argon gas, which produces an argon plasma flame at the torch (Jarvis *et. al.* 2003, 10).

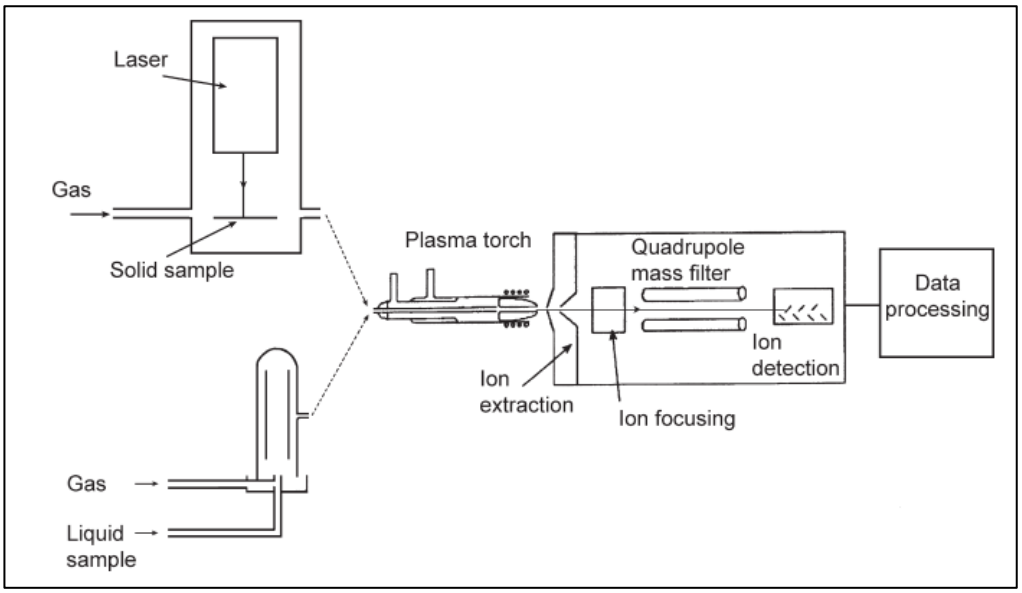


Figure 4.3 - Schematic Representation of ICP-MS procedure (after Pollard *et. al.* 2007, 198)

4.1.3 Nebulisation

The majority of ICP-MS analysis is performed on liquid samples; however this liquid needs to be converted into a gas stream to get the sample into the plasma (Williams 2003, 58). The role of the nebuliser is to aerosolise the sample prior to introducing it to the plasma. A coarse aerosol is created by mixing the liquid sample with Argon gas within a nebuliser. The aerosol needs to be composed of small droplets before being introduced to the Argon plasma; larger droplets are removed by a spray chamber (Figure 4.4).

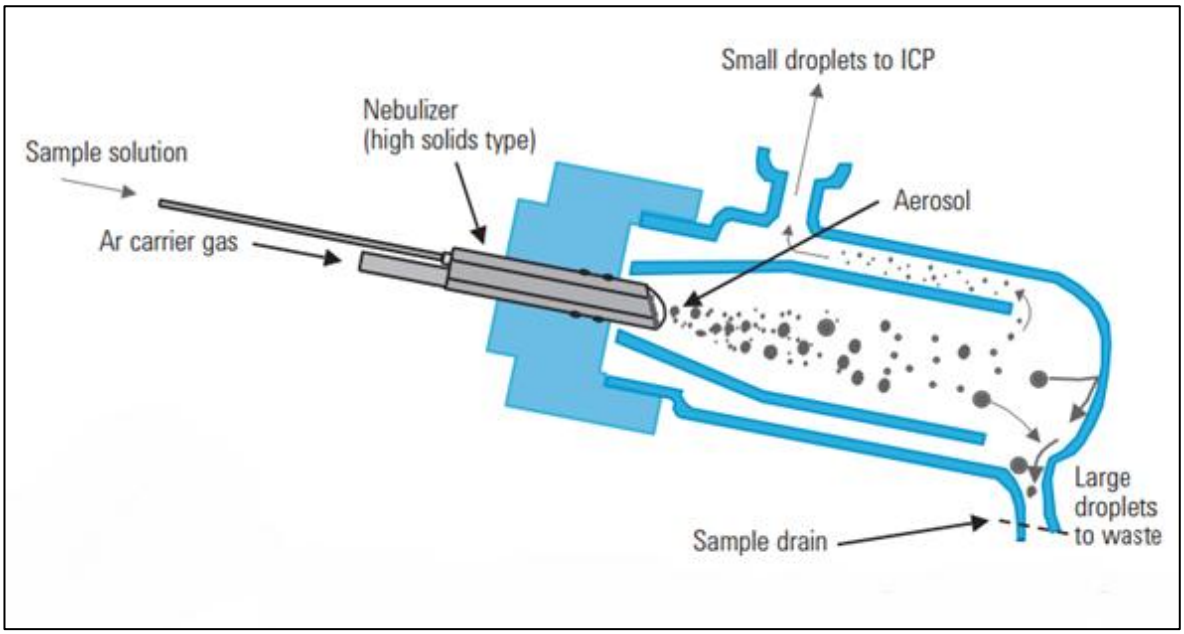


Figure 4.4 - Schematic of a nebuliser used in ICP-MS (Agilent Technologies 2005, 11)

4.1.4 Desolvation, atomisation and ionisation

The aerosolised sample is introduced to the plasma torch (Figure 4.5) which is sufficiently hot to desolvate, atomise and ionise a sample (between 6,000 - 10,000°C) (Mariet 2011).

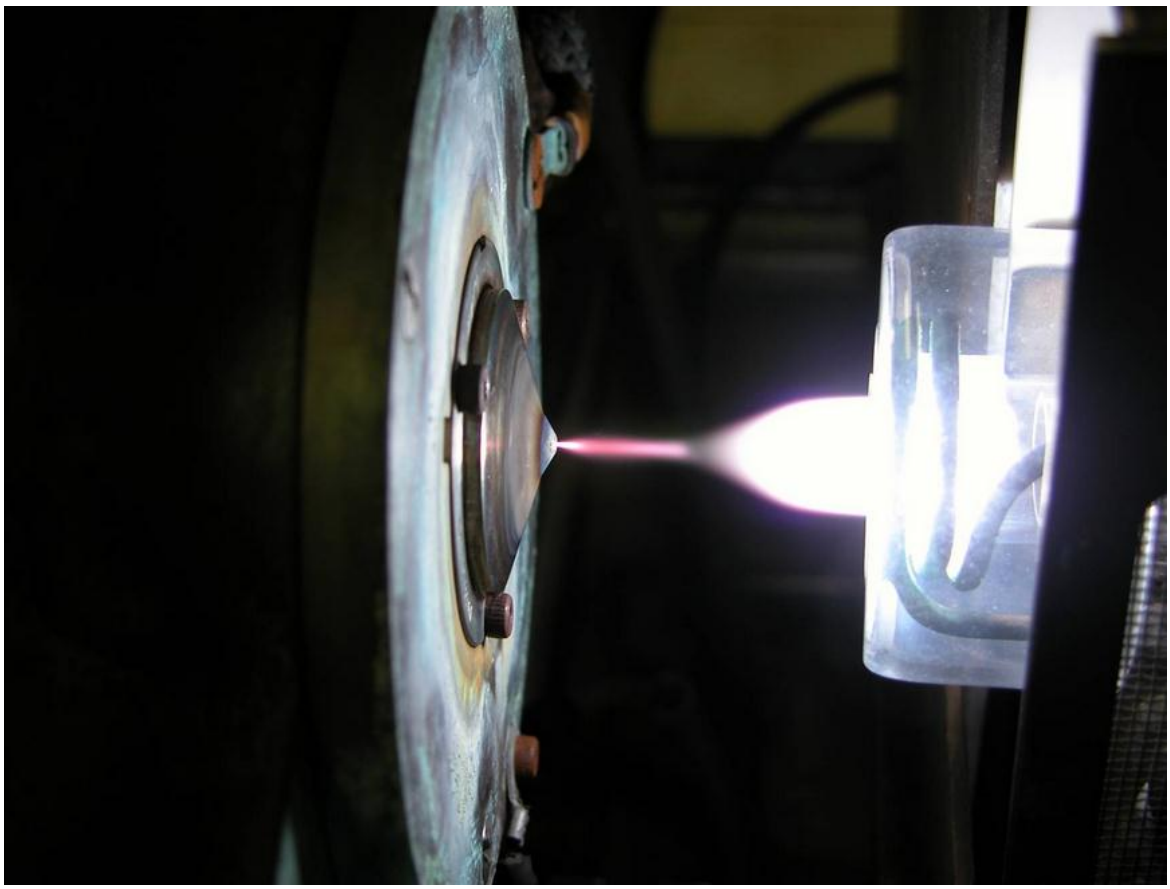


Figure 4.5 - Plasma flame at the skimmer cone aperture (Mariet 2011)

The aerosolised sample approaches the plasma and the surrounding water molecules are evaporated, leaving behind a small solid particle. This process is known as desolvation. The solid particle moves further into the plasma and is changed into a gas, and then into an atom (atomised). This atom is ionised through collisions with argon electrons, and the resulting ion is directed into the interface of the mass spectrometer (Thomas 2001, 30).

4.1.5 Mass analysis

The ionised sample then passes through the inductively coupled plasma and mass spectrometer interface. This interface is crucial as it forms a link between the high

temperature, atmospheric pressure plasma and the mass spectrometer, which is maintained in a vacuum. This interface is comprised of sampler and skimmer cones (Figure 4.6).

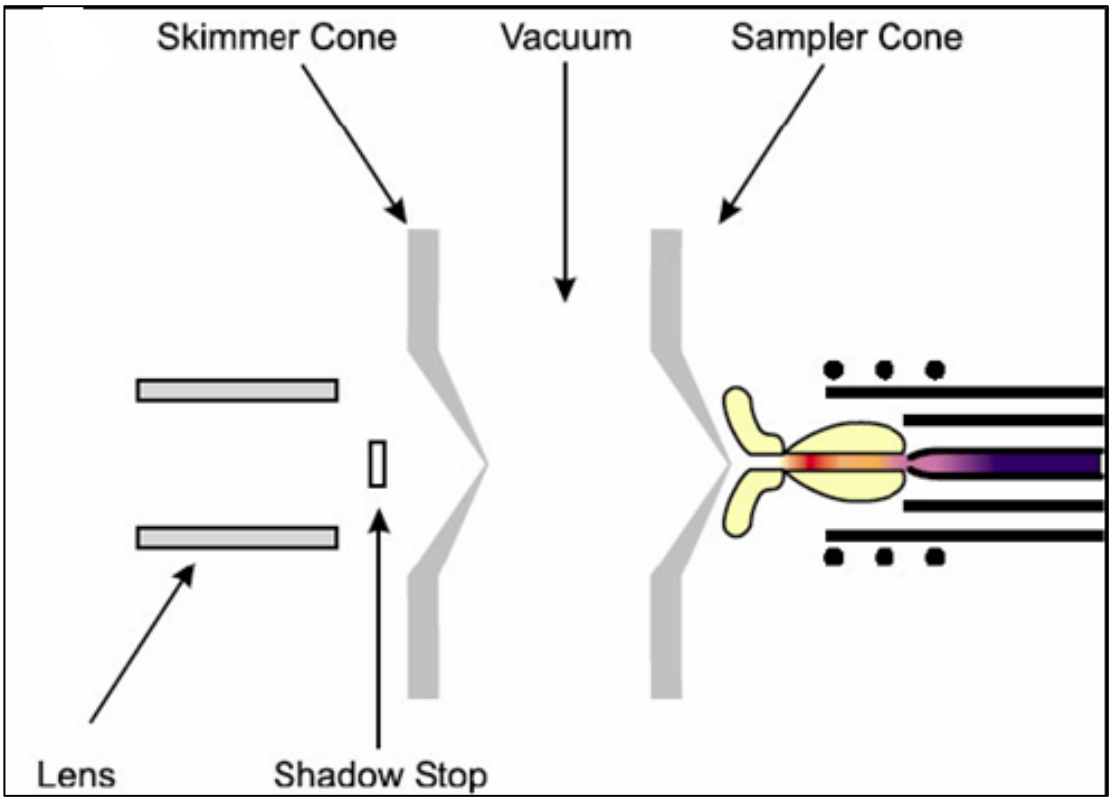


Figure 4.6 - Path of ionised sample (right to left) through the ICP-MS interface (PerkinElmer 2011)

The function of the sampler and skimmer cones is to form an interface between the plasma and the mass spectrometer without sacrificing sensitivity. The sampler cone is placed close to the plasma flame, and the difference in pressure between the plasma and the area behind the sampler cone draws ions through the small orifice of the cone (~1mm) (Dean 2005, 95). As the gas flow through the sampler cone is quite large, the skimmer cone is placed closely behind the sampler cone to permit only the passage of the central portion of the plasma gas and ion jet, as well as achieving a two-step reduction in the pressure between the plasma and the mass spectrometer (Perkin Elmer 2008, 3).

After passing through the interface, the ions travel towards a mass filter, which will separate ions with different masses. The most commonly used mass filter is a quadropole analyser (Figure 4.7), which consists of four metal rods, parallel to and equidistant from each other (Dean 2005, 96). Direct current (DC) is placed on one pair of rods and a radio frequency field (RF) is applied to other pair. This creates a situation where the DC and RF voltages can be manipulated to electrostatically steer ions of a selected mass to the ion detector, and ejecting unwanted ions from the quadropole (Thomas 2001, 44).

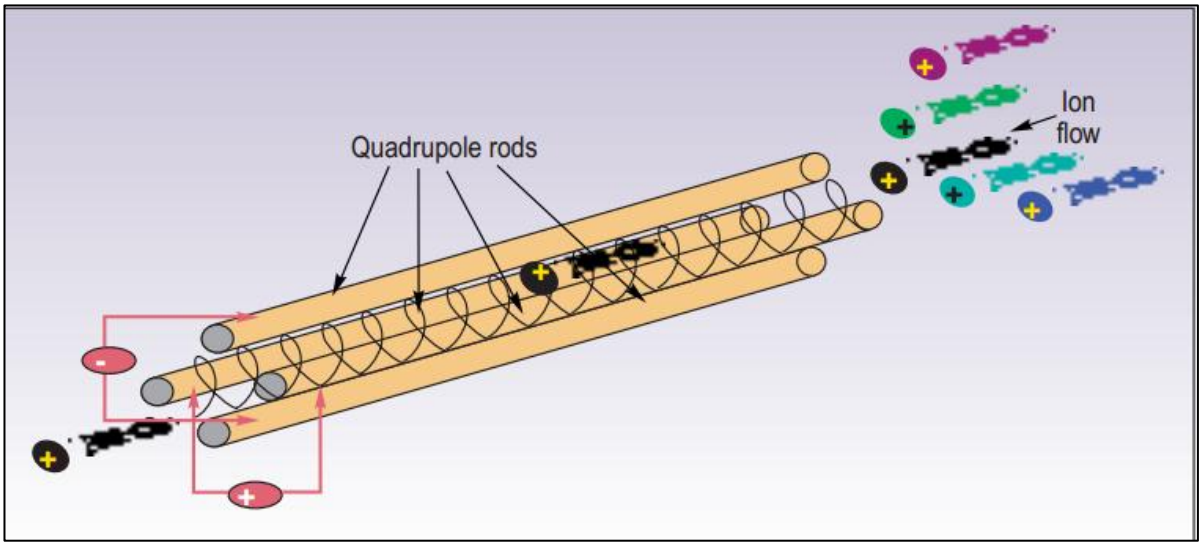


Figure 4.7 - Schematic diagram of a quadropole mass filter (after Thomas 2005, 45)

The quadropole mass filter can repeat this process, continuously changing the DC and RF values, for another analyte with a different mass until all desired analytes in a multielement analysis have been detected (Dean 2005, 97).

The ion, having passed through the quadropole mass filter, is converted into an electrical impulse by the detector. The detector is a horn-shaped tube (Figure 4.8) which has the opposite charge to that of the ions being detected. This attracts the ions leaving the quadropole, which collide with the surface inside the detector. This collision causes the

emission of secondary electrons, which travel further into the tube, emitting yet more electrons as they collide with the interior of the detector. This multiplication continues, resulting in up to 10^8 electrons being collected - this discrete pulse of electrons is amplified further and recorded as a number of ion counts per second (Dean 2005, 103-4; Jarvis *et. al* 2003, 48-50).

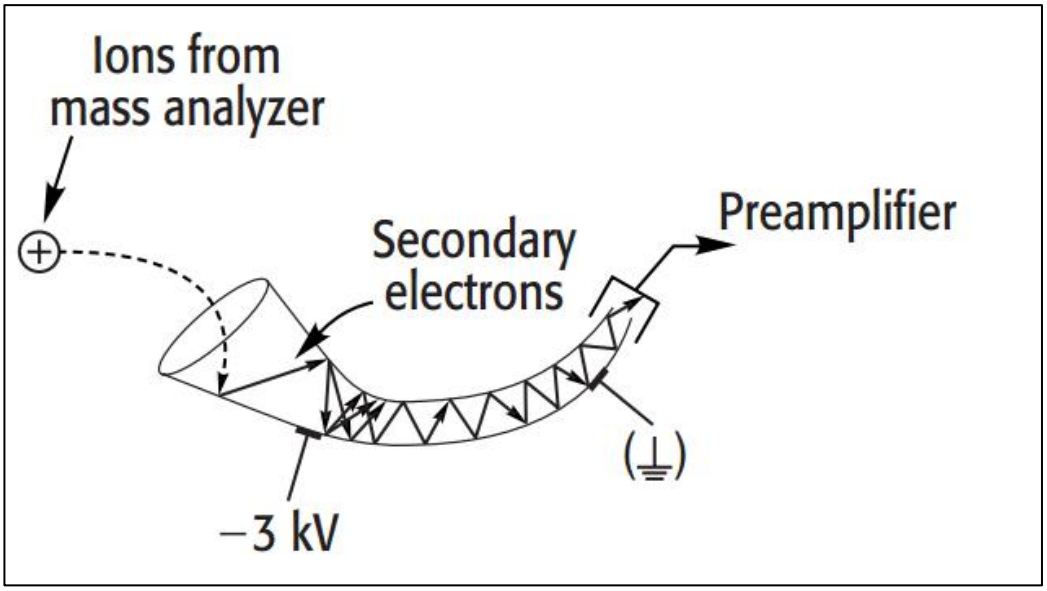


Figure 4.8 - Detector, showing path of secondary electrons (Thomas 2002, 35)

ICP-MS accurately quantifies how much of a specific element (or elements) is in the initial sample. In order to display the data gathered, computer software is required to analyse the data and monitor the mass spectrometer.

4.1.6 Comparison of LA-ICP-MS and acid digestion ICP-MS

Laser ablation ICP-MS and acid digestion ICP-MS are both suitable procedures for this study, however there are a number of advantages and disadvantages, predominantly in relation to sample preparation (Tables 4.1 & 4.2).

Laser ablation ICP-MS	
Advantages	*Disadvantages*
● Minimal preparation. ● Virtually non-destructive, suitable for use on rare/significant samples, i.e. archaeological artefacts. ● Can track changes across a sample. ● Much quicker than acid-digestion ICP-MS	● Sample must fit into sample chamber, may require subsampling. ● Potentially hazardous (laser) ● Ablation products may not be representative of the sample, as only the surface is being ablated. ● Cannot determine same range of elements as acid digestion ICP-MS. ● Matrix effect

Table 4.1 - Advantages and disadvantages of LA-ICP-MS

Acid digestion ICP-MS	
Advantages	*Disadvantages*
● No sample size limit. ● Highly sensitive, can detect a wide range of elements. ● Results representative of sample analysed.	● Potentially hazardous (acid, furnace). ● Only a small amount required, but is totally destructive. ● Time consuming. ● Loses spatial information within the sample. ● Bulk analysis of sample, may lose finer changes across a sample/artefact

Table 4.2 - Advantages and disadvantages of acid digestion ICP-MS

For this project, both LA-ICP-MS and acid digestion ICP-MS have significant advantages. The characterisation of geological sources of flint can be best achieved through acid digestion; the

greater sensitivity of this approach will allow for the detection of a wider range of elements, and destruction of geological samples is not problematic. This project will then compare the results obtained from geological sources to archaeological artefacts. While acid digestion is more sensitive, LA-ICP-MS is likely to be more attractive in terms of testing items from museum collections or 'one of a kind' artefacts as it is virtually non-destructive (the scar from the laser can be viewed under magnification). However, LA-ICP-MS would still require subsampling of the artefact as it must fit into the analysis chamber – a process that would be more destructive than the actual analysis. LA-ICP-MS is also not as sensitive as acid digestion ICP-MS and cannot detect the same large range of elements. For these reasons, LA-ICP-MS was not used in this study as portable X-ray fluorescence spectrometry can achieve the objective of non-destructive analysis, without the need for subsampling of the artefact.

4.2 Portable X-ray fluorescence spectrometry

X-ray fluorescence spectrometry is a multi-element analytical technique commonly used in archaeology to determine the elemental composition of a variety of materials recovered during excavation (Herz & Garrison 1998, 47). In recent years, there has been an explosion of studies within archaeological literature using XRF to analyse ceramics (Speakman *et. al*. 2011); pigments (Vila & Centeno 2013) and stone tools (Högberg et. al. 2012; Hughes *et. al.* 2010; Gauthier *et. al.* 2012; Nadooshan *et. al.* 2013; Frahm *et. al.* 2014).

In XRF spectrometry the X-ray tube within the instrument emits primary X-rays, which bombard the atoms on the surface of the specimen. The electrons occupy fixed orbits around the nucleus, analogous to the concentric orbits of planets within the solar system, and these orbits have fixed energy levels (Pollard *et. al.* 2007, 230). These layers of orbiting electrons are

often referred to as ‘shells’, where K, L and M are successive electronic shells (K being nearest the nucleus) (Herz & Garrison 1998, 222). When the primary X-ray collides with an atom in the specimen, it disturbs the electrons orbiting the atom, causing an electron from a low-energy level to be ejected thus creating an empty space. An electron from a higher-energy shell then falls out of orbit to occupy this space. The difference in energy produced by the electron as it moves between shells is emitted as secondary X-rays, which are characteristic of the element. Secondary X-rays are counted and their energy is measured, allowing the elements contained within the sample to be identified and quantified (Pollard *et. al.* 2007, 101).

XRF spectrometry can detect multiple elements simultaneously; however the range of elements that can be detected varies. Under normal operating conditions, XRF can detect elements between Magnesium and Uranium (inclusive) (Liritzis & Zacharias 2010, 115). For elements with a lower atomic number than Magnesium, XRF analysis can be conducted in a vacuum to counteract the effect of the surrounding air absorbing the secondary X-rays (Pollard *et. al.* 2007, 106).

Like LA-ICP-MS, XRF measures the elemental composition of the surface of a sample. This may lead to difficulties in analysis where a sample is heterogeneous, as differences in the overall chemical composition of the sample may not be detected. Unless the surface is of specific interest, this problem can be surmounted by careful preparation of the sample, i.e. obtaining a core from the sample, or removing a portion of the sample to expose the material beneath the surface. For this reason, XRF is most suitable for samples which are relatively homogeneous. The correct preparation of the sample can minimise the difficulties inherent in surface analysis. For XRF, the sample surface must be relatively flat and free from obvious contamination. An irregular surface alters the path of the secondary X-rays, leading to inaccurate results (Högberg *et. al.* 2012, 228). In this regard, flint is a particularly accommodating material as a large

nodule can be knapped into smaller flakes, which have flat surfaces ideal for analysis. Each of these flakes can be analysed any number of times, providing information about the chemical composition of different areas of the same nodule. However, care must be taken to avoid areas of staining, and calcareous or fossil inclusions within the flint as these will not be representative of the raw material. Patina can form on the external surface of flint as a result of weathering and/or depositional environment. Provided the sample is large enough, this patinated layer can be removed through careful knapping.

XRF has proved useful in the chemical characterisation of flint from a variety of Swedish and Danish sources (Hughes *et. al.* 2010; Högberg *et. al.* 2012). The advantages and disadvantages of this approach are summarised below (Table 4.3):

X-ray fluorescence	
Advantages	*Disadvantages*
● Non-destructive ● Quick (as little as 10 seconds) ● Minimal sample preparation ● No limit on sample size ● Portable	● Surface analysis only, sample may not be representative ● Matrix effect ● Cannot detect as many elements as acid-digestion ICP-MS ● Potentially hazardous (X-rays)

4.3 Advantages and disadvantages of X-ray fluorescence

4.3 Previous provenancing studies

Baseline data for provenancing flint can be drawn from previously published studies investigating the geochemical variation found within and between flint outcrops. This data can be compared to results obtained from the pXRF and ICP-MS analyses conducted as part of this study. Previous studies have used an array of analytical methods to characterise flint from

Britain, Ireland, and continental Europe. These studies will be summarised, including identification of element(s) useful for differentiation between sources of flint. The following research varies in terms of detail provided regarding elemental concentrations or indeed elements that were identified as useful for provenancing, however where possible these are included to provide a foundation for comparison in later chapters.

Sieveking *et. al.* (1970) investigated flint samples from British and French axe production sites using atomic emission spectroscopy (AES) and atomic absorption spectroscopy (AAS). Twenty samples were obtained from each site and analysed using AES, and AAS. Complete elemental concentrations were obtained for aluminium, magnesium, potassium, and iron from the samples analysed (Sieveking *et. al.* 1970, 254). Discriminant function analysis resulted in 85% of the individual flints being correctly classified; misclassification occurred with samples from geographically proximate sites (e.g. Black Patch and Cissbury) (*ibid*.). When these sites are combined classification accuracy increased to 95%.

The study conducted by Sieveking *et. al.* (1970) is a significant milestone in the field of geochemical provenancing, however the numbers of sites sampled (six) and complete concentrations of elements (four) is rather restricted. Elemental concentrations are unfortunately not provided, giving no indication regarding quantities of element(s) found at each site, although aluminium appears to be significant for differentiation between sites in Britain and on continental Europe. It is also temporally confined, focusing solely on Neolithic axe production sites. Despite these issues, the study demonstrates that differentiation of flint sources using geochemical analysis is possible. The authors are clear that this study represents a preliminary foray into the geochemical investigation of flint and that increased numbers of samples are required, as well as data from additional elements (Sieveking *et. al.* 1970, 254).

Building on these results, Sieveking *et. al.* published another study in 1972 which included a reanalysis of the material investigated previously, in addition to samples obtained from two adjacent flint mines in Holland (St. Geertruid and Rijckholt) (Sieveking *et. al.* 1972, 154). The 1972 publication outlines analysis where concentrations were detected and quantified for eight elements: calcium, magnesium, aluminium, iron, sodium, lithium, potassium, and phosphorus (Sieveking *et. al.* 1972, 160). Each element measured had a normal distribution indicating that the flint from each site formed a homogeneous group (Sieveking *et. al.* 1972, 160). Discriminant function analysis was used to establish groups of flint mine products and to classify unknown objects into a group; for this statistical analysis the data relating to 99 of the flint samples were treated as 'unknown' to determine if they can be accurately provenance using the data collected from each site. Classification for British and European samples was 80% correct, however when analysed separately the samples from British sites were correctly classified 94.8% of the time (Sieveking *et. al.* 1972, 163).

The mean concentration (ppm) of each of the eight elements detected from each English site is presented below (taken from Sieveking *et. al.* 1972, 166-9):

	Mean element concentration (ppm)							
	Al	Fe	Mg	K	Na	Li	P	Ca
Grime's Graves	665	84	25	235	288	6	91	949
Easton Down	259	68	37	206	233	25	125	7519
Black Patch	338	88	30	173	134	20	80	5791
Cissbury	301	118	39	162	208	13	62	4547
Peppard	472	104	29	281	287	17	98	2878
Beer	1297	257	67	454	396	19	330	2726
Clanfield	217	37	34	113	131	9	67	2699

Table 4.4 – mean concentration (ppm) of elements quantified from British flint sources (Sieveking et. al. 1972)

Immediately obvious from the data presented in table 4.4 is the variation in the concentration of some elements between different sources, for example the much higher concentration of iron in samples from Beer compared to other locations.

In building on the preliminary results of the 1970 publication, Sieveking *et. al.* have increased the number of sites under investigation and demonstrated that increasing the number of elements under investigation will assist with distinguishing between sites. However the temporal and geographic range of this study is still rather narrow, as only ten sites were sampled and the focus remains on Neolithic axe production and associated raw material mining. The results of the analysis are provided, giving quantities of each element in ppm, as

well as details of the archaeological and geological contexts of the samples and artefacts analysed (Sieveking *et. al.* 1972, 166-75). This data provides a valuable baseline for future investigation and can be compared to the results obtained in this study using pXRF and acid digestion ICP-MS.

The flint artefacts analysed by Sieveking *et. al.* (1970) were reanalysed using neutron activation analysis (NAA) by Aspinall & Feather (1972), with the anticipation that NAA would yield a greater range of elements for use in geochemical provenancing due to the increased sensitivity of the method (Aspinall & Feather 1972, 41). Aspinall & Feather also investigated (in)homogeneity of several flint samples by retesting them months after the initial irradiation; while these tests were not extensive enough to reveal the inhomogeneity of flint, they were satisfactory as a test for experimental reliability of analysis (Aspinall & Feather 1972, 46). The mean concentration values of these elements and elemental ratios from each site were compared to the results obtained from the Cissbury samples, which was arbitrarily chosen as a 'standard' site (Aspinall & Feather 1972, 48).

Mean concentration of elements detected in Aspinall & Feather are presented below (data from Aspinall & Feather 1972, 47):

	Element concentration (ppm)						
	Cs	Sc	Ta	Cr	Th	U	Fe/Co
Cissbury	0.013	0.11	0.005	0.6	0.043	0.23	860
Black Patch	0.03	0.11	0.004	0.6	0.08	0.2	1600
Grime's Graves	0.023	0.23	0.012	0.7	0.14	0.8	3000
Easton Down	0.011	0.10	0.005	0.6	0.07	0.16	360
Peppard	0.013	0.19	0.001	0.6	0.07	0.17	760

Table 4.5 – Mean element concentration from flint collected from British flint mine sites (taken from Aspinall & Feather 1972, 47)

The analysis in Aspinall & Feather highlighted differences between sites using a suite of trace elements. Compared to the analysis conducted in Sieveking *et. al.* (1972) there are no common elements quantified so comparison is difficult. However the data provided in Aspinall & Feather can be contrasted with results obtained from future analyses.

Using the percentage of element concentration data points within one standard deviation of mean values to create a 'range' of element concentrations indicative of a particular source, Aspinall & Feather used the data from six samples as 'unknown' and attempted to identify their origin, four from Britain and two from continental sites. All but one sample was correctly classified: the sample in question was collected from Black Patch, but fell within the ranges for

either Cissbury or Black Patch – echoing the results of the analyses conducted by Sieveking *et. al.* (1970 & 1972) which demonstrated that sites clustered on the South Downs may potentially be more difficult to separate geochemically, although it was possible.

The experiments conducted by Sieveking *et. al*. (1970, 1972) and subsequent discriminant function analysis found that flint from British sites could be correctly classified 94.8% of the time (Sieveking et. al. 1972, 163), whereas Aspinall & Feather found that five out of six objects were correctly classified (c.83% classification accuracy) using comparison of patterns of element/element ratios to the arbitrarily chosen 'standard' of Cissbury. There is no geological or geochemical justification for the use of Cissbury flint as the benchmark to which other samples should be compared in order to investigate their provenance, and the numbers of samples (six) selected as 'unknown' to test the strength of pattern-matching for provenance is quite small compared to the 99 samples included in the discriminant function analysis undertaken in Sieveking *et. al.* (1972).

Investigation of flint from British and continental European sites continued in the work of Rockman (2003), who utilised LA-ICP-MS and acid digestion ICP-MS to obtain data from sources of raw material and archaeological artefacts. Each reading represents a single nodule; multiple readings for each area derive from different nodules collected from each location (Rockman 2003, 312), with the exception of one nodule which was tested multiple times to determine inter-nodule variability and to compare this with the variability within and between sources (Rockman 2003, 308).

The LA-ICP-MS analysis detected 39 elements and demonstrated greatest separation between the rare earth elements and transition metals; acid digestion ICP-MS (which is substantially more precise) therefore focused primarily on rare earth elements. Although the methods

utilised here are not combinable, both techniques returned similar results on the same samples, suggesting that the patterning in the results of one technique can be compared to the results obtained from the other (Rockman 2003, 334-5). Discriminant function analysis was conducted to test the strengths of the established sample collection groups and to test the classification of archaeological artefacts. This analysis demonstrated that at least four areas of Britain where flint occurs can be distinguished geochemically: southwestern chalk flint, southwestern clay-with-flints, northeastern chalk flint, and southeastern chalk flint (Rockman 2003, 348). Rockman provides details of which elements are most useful when distinguishing between sources of flint using both LA-ICP-MS and acid digestion ICP-MS, but not the raw data obtained from these analyses. For LA-ICP-MS, the most useful elements are rubidium, lanthanum, uranium, and praseodymium, whereas lutetium, rubidium, and barium are most useful for separating source groups with data obtained from acid digestion ICP-MS (2003, 348).

The analysis conducted by Rockman provides a useful comparison between two different analytical approaches and indicates that flint sources in Britain can be distinguished geochemically. Using two methods, one destructive and one quasi-non-destructive, was particularly apposite as the analysis of archaeological artefacts is frequently limited by the anticipated damage caused during the investigative process.

Investigation of flint from Britain continued with the work of Durst (2009), who utilised LA-ICP-MS to investigate the provenance of raw material used for gunflint manufacture. No raw data is provided in the publication. Although 45 elements were detected using LA-ICP-MS (Durst 2009, 26), only aluminium and uranium are used here for the purposes of differentiating between sources. Durst is clear that this study represents a preliminary foray into geochemical sourcing of gunflints and acknowledges that many more samples are required to characterise with good confidence the different areas of flint occurrence in Europe and Britain (Durst 2009,

29). Interestingly, aluminium concentration is highlighted here as one element useful for geochemical provenancing, as was previously identified in Sieveking *et. al.* 1970 & 1972.

Although outside the study area of this research, a series of studies on Scandinavian flint investigated the geochemical variability of flint from continental Europe. Beginning with a pilot study in Hughes *et. al.* (2010), samples of flint from Denmark and Sweden were analysed in solution with ICP-MS, inductively coupled plasma-optical emission spectroscopy (ICP-OES), and in solid form with LA-ICP-MS and energy dispersive X-ray fluorescence (EDXRF). The results revealed that the samples were chemically homogeneous within each respective layer or locality, while the layers and localities were differentiated from each other (Hughes *et. al.* 2010, 21). Hughes *et. al.* state that further sampling and increasingly detailed analyses would be necessary to provide definitive geochemical compositions of sources using ICP-MS and ICP-OES (*ibid*). For these reasons, in addition to the regrettably destructive nature of both ICP-MS and ICP-OES, EDXRF was trialled on 50 samples. The comparison of calcium, iron, and silica was conducted using ratios of integrated net peak intensities, not quantitative comparison. The analysis resulted in provisional chemical groupings which appeared to be geographically discrete (Hughes *et. al.* 2010, 22). The groups established were based purely on the basis of the similarity of calcium and iron readings, with adjacent sites placed into different groups, indicating that geographic proximity does not necessarily mean geochemical similarity. The results also indicate that flints of similar appearance can have markedly different chemical signatures, and flints from different geological ages from the same location can share a chemical signature (Hughes *et. al.* 2010, 22).

Following from this qualitative pilot study the samples in Hughes *et. al.* 2010 (and additional geological samples) were reanalysed and fully quantified using EDXRF; it became clear that differentiation based on the ratios of two elements (calcium and iron) was not sufficient, and

that investigation of intra- and inter-source variability will require further sampling and quantification of other elements (Hughes *et. al.* 2012, 792). The authors also acknowledge that some of the additional localities are represented by very small numbers of samples (*ibid.*).

The mean quantitative composition estimates for samples analysed in Hughes *et. al.* 2010, and subsequently reanalysed by Hughes *et. al.* 2012, are presented below:

	Element concentration (ppm)						
	Denmark/SW Sweden			**SW Sweden**			**SE Sweden**
	Södra Sallerup	Møns Klint	Stevns Klint	Klagshamn	Östra Torp	Smygehuk	Hanaskog
Al_2O_3	1680	1010	1740	780	360	1020	1310
SiO_2	995000	994400	991700	950100	951300	967000	989400
SO_3	230	255	250	60	25	25	300
Cl	87	52.2	258	134	98.6	154	51.6
K_2O	260	265	215	400	840	780	420
CaO	1470	1365	397.3	45300	45300	40900	6120
Ti	23.2	32	37	63.8	58.8	92.6	79.8
Mn	N.C.	N.C.	3	5.4	5.6	8.8	3.6
Fe	75.7	62.1	92.7	147.7	168.2	208.9	378.6

Table 4.6 – mean composition estimates from Swedish and Danish flint sources (after Hughes *et. al.* 2012, 784, N.C. = not computed).

The results in table 4.6 illustrate the differences in geochemical composition of flint from the different source areas identified in Hughes *et. al.* 2010. Using these results it was possible to differentiate between sources through comparison of iron and calcium; however differentiation between Danian and Senonian layers of flint at Stevns Klint could be achieved using variation in chlorine composition (Hughes *et. al.* 2012, 791).

Forty-five of the original samples from Hughes *et. al.* (2010) were reanalysed by Högberg *et. al.* (2011) using EDXRF and the same chemical groupings were established using variation in the concentration of calcium and iron (Högberg *et. al.* 2011, 230). The authors concede that further sampling is required, as well as quantification of other elements (*ibid.*).

The most recent attempt to investigate the geochemical variation of flint in Britain focused on Magdalenian artefacts and procurement and movement of material (Pettitt *et. al.* 2012). This study built on the work completed by Rockman (2003) and used LA-ICP-MS to analyse artefacts and geological samples (Pettitt *et. al.* 2012, 278-280). Ten nodules were collected from each locality and knapped into smaller flakes, which were analysed on three separate areas; therefore each sample was characterised by nine measurements and each source by 90 measurements (Pettitt *et. al.* 2012, 280). The artefacts were each ablated in nine different locations, the median measurements for each element were used to compare the composition of the artefacts to the different source areas (*ibid.*). Characterisation of artefacts and source areas was completed using canonical discriminant analysis (CDA), which suggested that the finest resolution possible was a regional scale – the source areas differentiated were southwestern Chalk (Salisbury Plain/Beer), southeastern chalk flint (South Downs), northeastern Chalk flint (North Lincolnshire bedrock flint), and southwestern clay-with-flints (also Beer Head area) (Pettitt *et. al.* 2012, 285). The elements that were most useful for differentiation between the source regions were aluminium, potassium, rubidium, zirconium,

niobium, and barium (Pettitt *pers. comm.*). These elements, and the concentrations detected, were not included in the original publication.

In summary, the studies outlined above investigating the geochemical composition of flint from Britain and continental Europe have demonstrated that variability does exist between different sources. The analyses conducted by Sieveking *et. al.* 1972 and subsequent reanalysis of the same samples in Aspinall & Feather 1972 each outlined the potential of trace elements to distinguish between different sources of flint using different analytical techniques. The elements under investigation in each of the studies vary due to the inherent differences with regards instrumental sensitivity; neutron activation analysis was employed by Aspinall & Feather with the deliberate aim of yielding additional elements for provenancing, supplementing the more abundant elements quantified by Sieveking *et. al*. 1972. Some sites appeared to have particular elemental 'signatures' that may be of use in future provenancing work; samples analysed from Grime's Graves were found to have higher concentrations of scandium and uranium, postulated as arising from variability in the depositional environment during the Late Cretaceous (Aspinall & Feather 1972, 53). It is suggested elsewhere that areas of chalk deposition that were located on the margins of the Cretaceous chalk basin, e.g. Beer, are likely to be more distinct (i.e. have greater variation in trace elements) than those in the centre, such as Cissbury (Bush & Sieveking 1986, 134; Rockman 2003, 345-7).

The analysis of results in Sieveking *et. al.* (1972) was completed using discriminant function analysis using data gathered from eight elements, whereas Aspinall & Feather (1972) used mean values of elemental concentration and standard deviation to measure the spread of individual elements from site to site. Aspinall & Feather have compared the results from other sites to the results obtained from Cissbury, arbitrarily chosen as 'standard'. This creates difficulties when evaluating this study in light of more recent attempts at provenancing which

look at individual sites in relation to each other or adopt a broader resolution, e.g. regional scale.

A number of studies have suggested that provenancing flint on a regional scale is perhaps the most appropriate. Low-resolution provenancing has been demonstrated in Sieveking *et. al.* (1970, 1972) and Aspinall & Feather (1972) where differentiation between British and continental European sources of flint was readily achieved. However LA-ICP-MS analysis outlined in Durst (2009) indicated that there was a significant degree of overlap between flint samples collected from Britain, France, and Denmark (Durst 2009, 25). Following their analyses of Scandinavian flint, Hughes *et. al.* (2012, 793) and Högberg *et. al.* (2012, 234) add a note of caution for provenancing studies by noting that chemical similarity between different flint samples does not necessarily mean that the sources of flint will be proximate. Flints which share a geochemical signature may outcrop some distance from each other, whereas flints collected from nearby locations may differ significantly in terms of their chemical composition.

4.4 Summary

This chapter has provided an overview of inductively coupled plasma mass spectrometry, with reference to both laser ablation and acid digestion, as well as X-ray fluorescence. There are considerable differences between the sample preparations for these procedures, with the potential for introduction of contamination being the main threat to accurate analyses. The mechanical reduction necessary for acid digestion adds time and could introduce contamination. However, the potential for greater accuracy using acid digestion ICP-MS makes it suitable for the geochemical characterisation of flint. Both LA-ICP-MS and XRF are surface analysis techniques, and neither can detect the same range of elements as acid digestion ICP-

MS. However, they are much more suited to the analysis of archaeological artefacts as LA-ICP-MS is minimally destructive, and XRF is non-destructive.

5.0 METHODOLOGY

This chapter outlines the methodologies used for pXRF and ICP-MS and the rationale behind sample collection and preparation. It will also cover the differing sample preparation for these approaches. The sample collection and analysis using ICP-MS and pXRF were designed around a set of specific research objectives:

1. To determine whether it was possible to identify the chemical composition of flint from primary outcrops, sampled from a number of areas with flint-producing Cretaceous chalk around Britain and Ireland. In Britain, these areas are the Northern, Southern, Transitional, and the Southwestern Chalk Provinces. In Ireland, the Northern Ireland Province contains the majority of flint-bearing chalk;

2. To assess whether it was possible to identify differences in the chemical composition of flint between and within these source areas and provide proof of concept;

3. To provide a comparison between pXRF and ICP-MS in achieving these objectives.

5.1 Sample Collection

Sampling locations were identified through a variety of different sources: geological literature (e.g. British Geological Survey, Geological Survey of Ireland); archaeological reports detailing presence of local sources of flint (e.g. Bradley & Leivers 2009, 13; Collins 1983, 6); previous provenancing studies (Pettitt *et. al.* 2012, 281; Rockman 2003, 312-20); as well as the author's own knowledge of flint outcrops in the north of Ireland. The aim was to characterise with good confidence a particular geographic area where flint outcrops above ground.

This study aimed to determine the chemical variation within flint sources in Britain and Ireland. Due to the limited geological occurrence of primary outcrops of flint, it was decided that focusing on these areas would be most appropriate to determine whether they can be geochemically distinguished using pXRF and ICP-MS. Secondary sources of flint are widely distributed, comingled, and have been eroded from multiple different primary sources, some of which are located underwater or in another country (Butler 2005, 17). Investigation of primary sources of flint enabled elemental characterisation of a discrete area, whereas analysis of secondary sources would provide multiple signatures and confuse attempts to gain a chemical 'fingerprint' of a particular area.

5.1.1 Sample locations

Sample collection from sites in Britain and Ireland was conducted over a number of excursions. The locations sampled are summarised in Table 5.1, full details, including GPS co-ordinates, are available in Appendix 5.1. Each location was photographed and GPS co-ordinates were taken at the location of each sample collected. Within each sample location, a variety of flint nodules were collected in order to obtain multiple readings from each source. The samples were sealed in unused plastic bags, and labelled with the name of the site, date, and GPS co-ordinates.

Site	Location	Samples Collected
A2, Dover	Kent, England	July 2013
Arras Hill chalk pit	East Yorkshire, England	March 2015
Ballintoy East	Antrim, Ireland	March 2013
Beer	Devon, England	July 2013
Brandon Country Park	Norfolk, England	July 2013
Carnlough	Antrim, Ireland	February 2014
Cissbury	West Sussex, England	July 2013
Cloughastucan	Antrim, Ireland	February 2014
Coast, Kent	Kent, England	July 2013
Eleven Ballyboes	Donegal, Ireland	September 2013
Field near Pewsey	Wiltshire, England	July 2013
A342, Pewsey	Wiltshire, England	July 2013
Garron Point	Antrim, Ireland	February 2014
Grime's Graves	Norfolk, England	July 2013
Hackpen Hill	Wiltshire	July 2013
Harrow Hill	West Sussex, England	July 2013
Isle of Wight Lane	Bedfordshire, England	July 2013
Kingston, Lewes	East Sussex, England	July 2013
Landpark Wood	Bedfordshire, England	July 2013
Malton	East Yorkshire, England	March 2015
Middleton Quarry	East Yorkshire, England	March 2015
Mill Hill Quarry	Lincolnshire, England	March 2015
Moon's Copse	Hampshire, England	July 2013
Murlough Bay	Antrim, Ireland	August 2013
North Landing	North Yorkshire, England	December 2014
North Ormsby chalk pit	Lincolnshire, England	March 2015
Portbraddan	Antrim, Ireland	March 2013
Rifle Butts Quarry	East Yorkshire, England	March 2015
Samphire Hoe	Kent, England	July 2013

Sledmere/Malton	East Yorkshire, England	March 2015
Slieve Gallion	Derry, Ireland	February 2014
Southwick Hill	West Sussex, England	July 2013
Stoke Down	West Sussex, England	July 2013
Welton-le-Wold	Lincolnshire, England	March 2015
West Kennet	Wiltshire, England	July 2013
White Park Bay	Antrim, Ireland	March/August 2013
White Rocks	Antrim, Ireland	March/August 2013
Winterbourne Stoke	Wiltshire, England	July 2013

Table 5.1 – Sample Locations in Britain and Ireland

A number of sites from provenancing work conducted by Pettitt *et. al.* (2012, 281) were resampled and can provide a comparison between this study and previously published results. These sites are located in the south of England and include: A2, Dover; Brandon Country Park; Pewsey; Harrow Hill; Moon's Copse; Samphire Hoe; Southwick Hill, and Isle of Wight Lane.

Figure 5.1 depicts the sampling locations within the Northern Ireland Chalk formation, with more detailed areas shown in 5.1a, 5.1b, and 5.1c. These samples were collected over four excursions (March, September, and August 2013, and February 2014), totalling five days in the field.

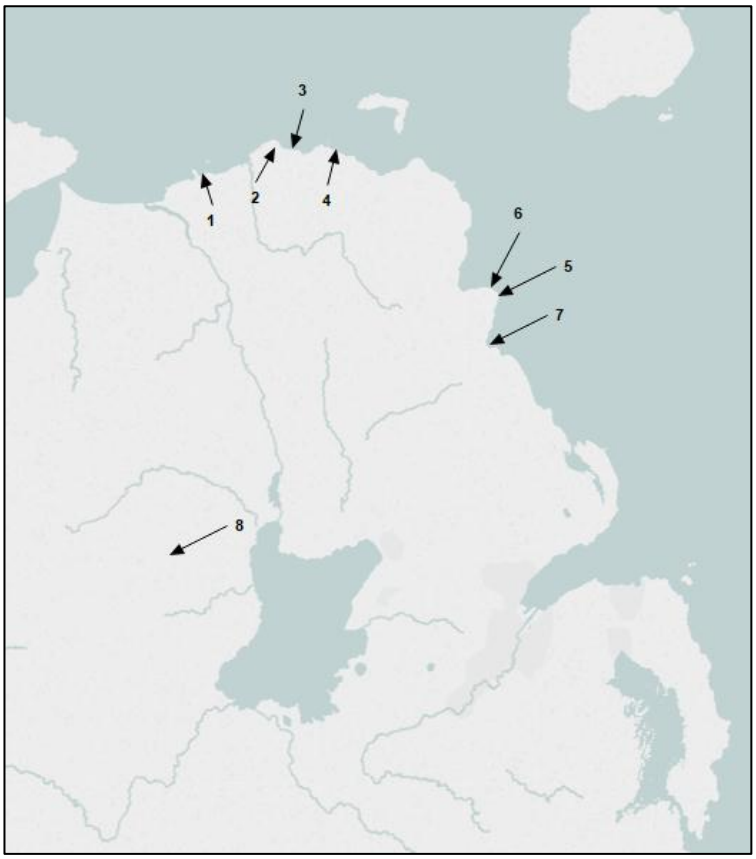


Figure 5.1 – Map of sampling locations in Northern Ireland (Tableau Software © 2016)

A more detailed view of sampling locations 1-4 is shown in figure 5.1a below. The Ulster White Limestone formation is shown in yellow.

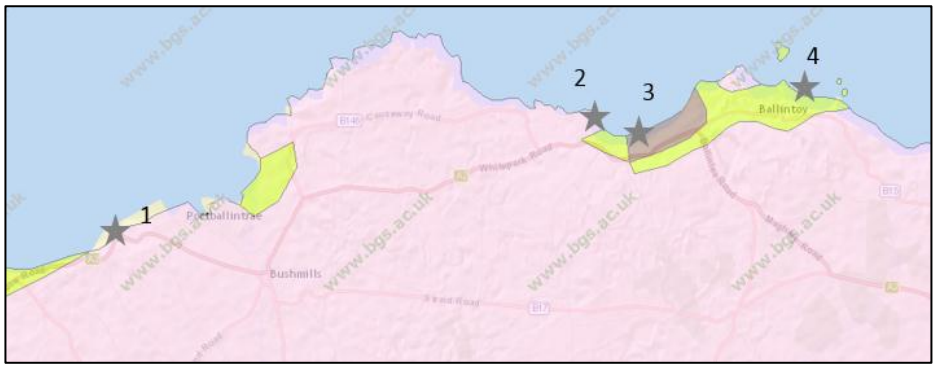


Figure 5.1a – Sampling locations 1: White Rocks; 2: Portbraddan; 3: White Park Bay; 4: Ballintoy East (Contains British Geological Survey materials © NERC 2015)

Sampling locations 5-6 are shown in figure 5.1b. As with above, the flint-bearing chalk formation is shown in yellow.

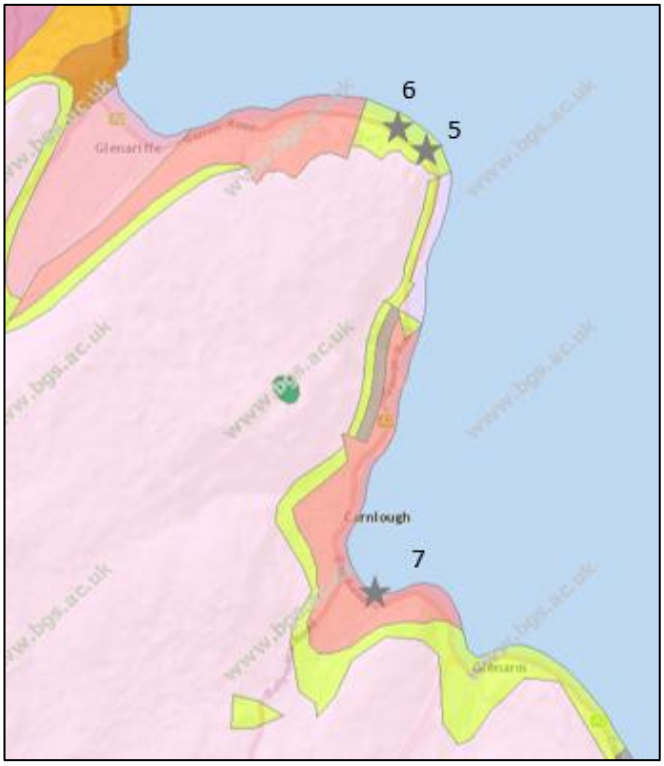


Figure 5.1b – Sampling locations 5: Garron Point; 6: Cloughastucan; 7: Carnlough (Contains British Geological Survey materials © NERC 2015)

The final sampling location is inland at a Cretaceous outlier located on the northern slope of Slieve Gallion (figure 5.1c).

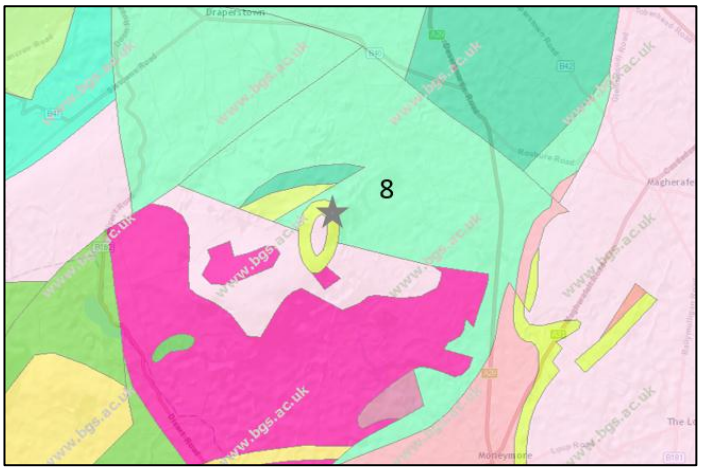


Figure 5.1c – Sampling locations 8: Slieve Gallion (Contains British Geological Survey materials © NERC 2015)

Figure 5.2 depicts the sampling locations in England. Sample collection in the Southern and Transitional Provinces took place over a week in July 2013, and three days in March 2015 were spent collecting samples in the Northern Province.

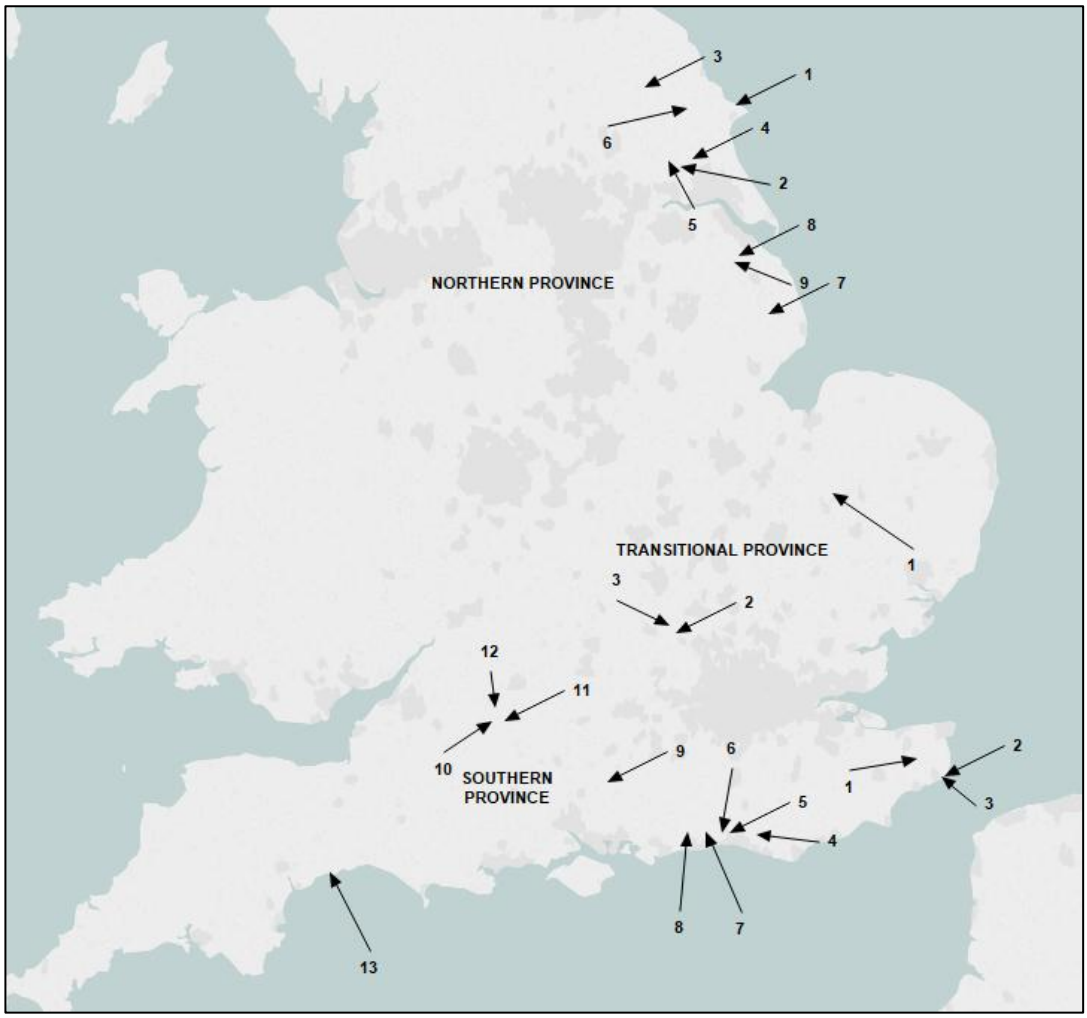


Figure 5.2 – Map of sampling locations in the Northern, Transitional, and Southern Chalk provinces (Tableau Software © 2016)

Figure 5.2a shows the sampling sites within the Northern Chalk province, focusing on the Yorkshire Wolds. Figure 5.2b displays the sampling locations in the Lincolnshire Wolds, also Northern province. The sampling sites in the Transitional Chalk province are displayed in figure 5.2c. Sampling sites in the Southern province are shown in figure 5.2d (North Downs), 5.2e (South Downs), 5.2f (Salisbury Plain/Pewsey), and 5.2g (Southwestern Chalk). The flint-bearing chalk geology is shown in yellow in the maps below.

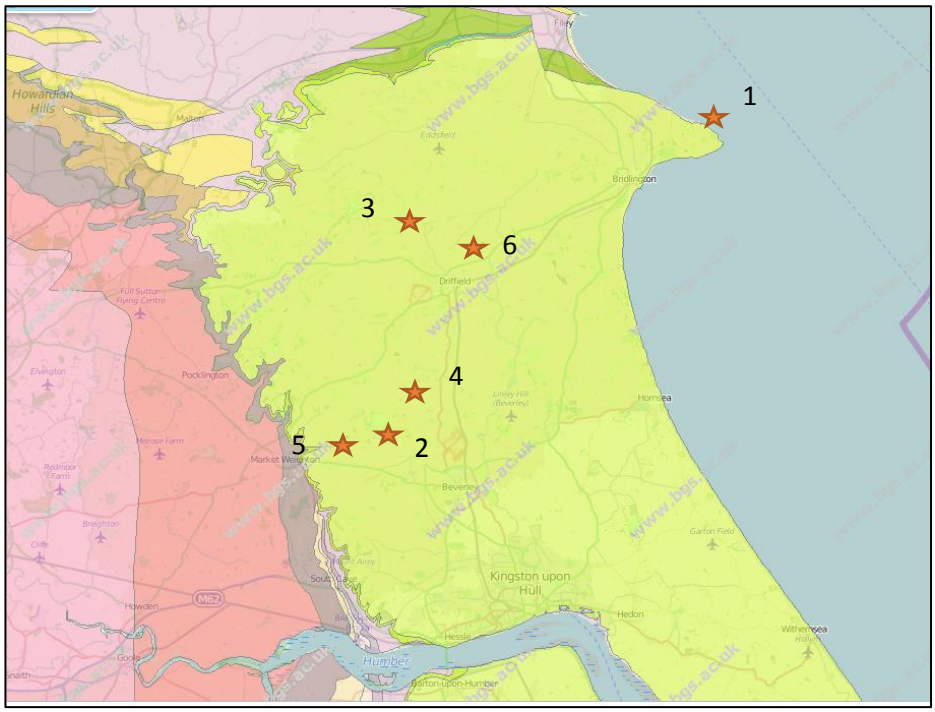


Figure 5.2a – Northern province sampling locations 1: North Landing; 2: Arras Hill; 3: Malton; 4: Middleton Quarry; 5: Rifle Butts; 6: Sledmere/Malton (Contains British Geological Survey materials © NERC 2015)

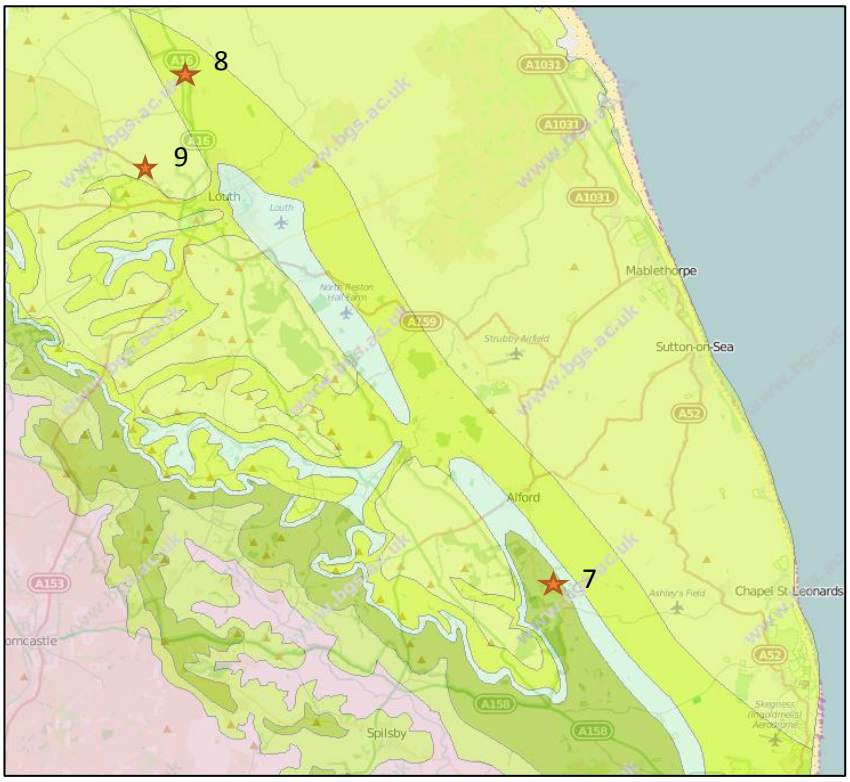


Figure 5.2b – Northern province sampling locations 7: Mill Hill; 8: North Ormsby; 9: Welton-le-Wold (Contains British Geological Survey materials © NERC 2015)

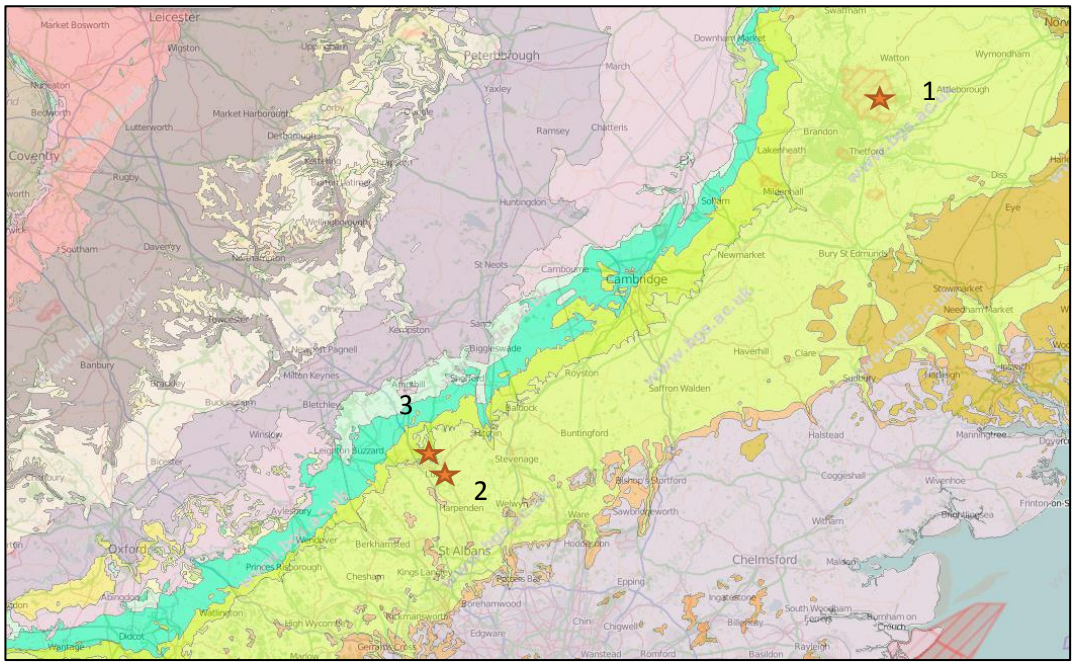


Figure 5.2c – Transitional province sampling locations 1: Grime's Graves; 2: Landpark Wood; 3: Isle of Wight Lane (Contains British Geological Survey materials © NERC 2015)

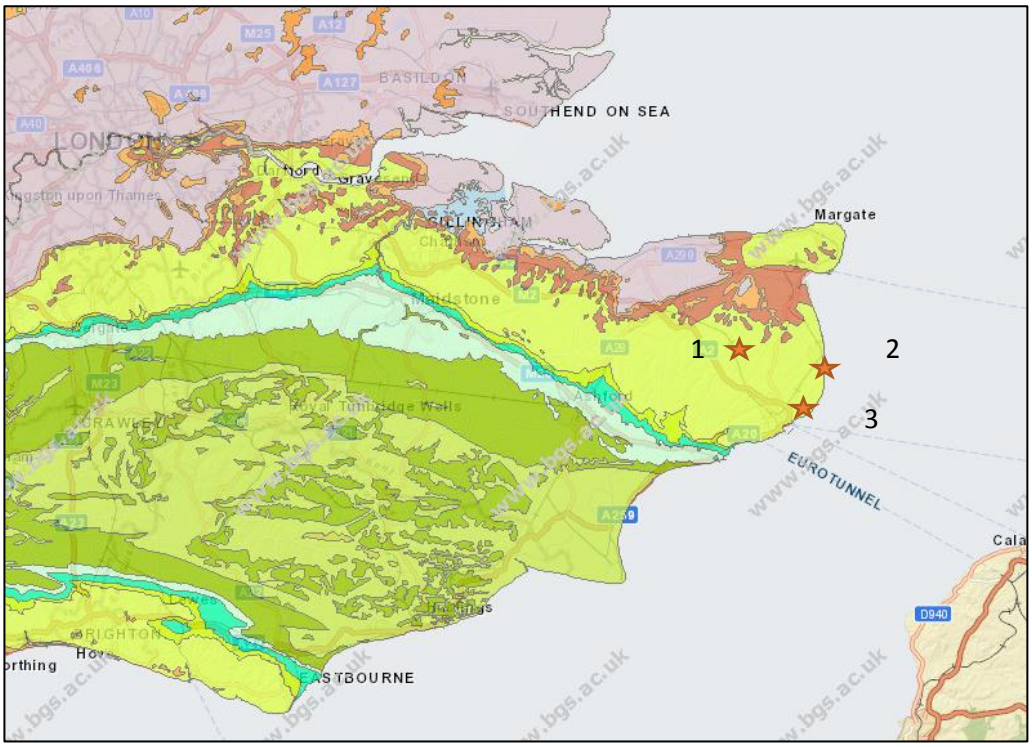


Figure 5.2d –Southern province sampling locations 1: A2 Ileden Lane; 2: Dover coast 1; 3: Dover Coast 2 (Contains British Geological Survey materials © NERC 2015)

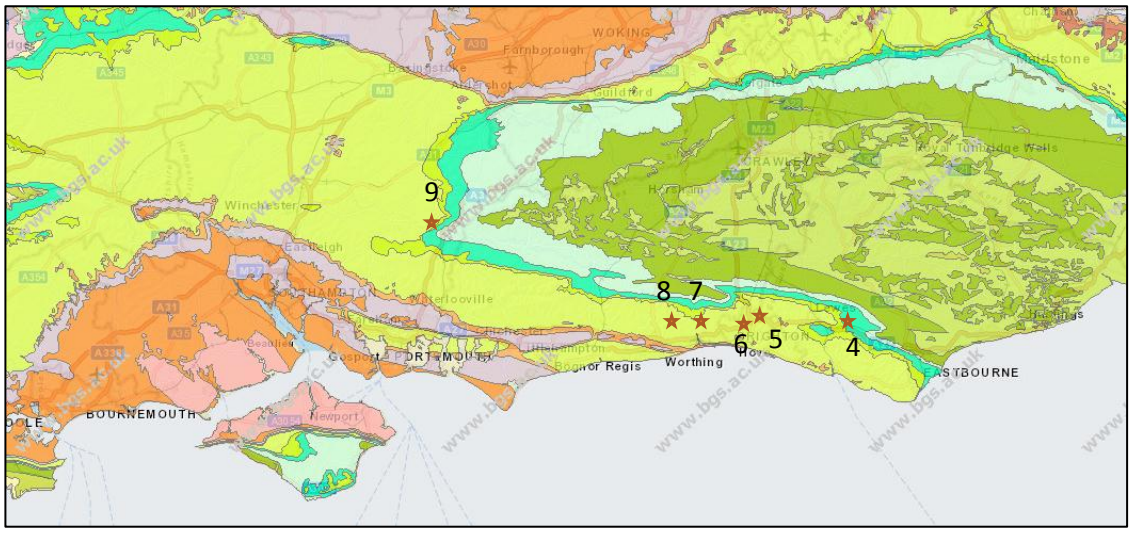


Figure 5.2e – Southern province sampling locations 4: South Downs Way at Kingston, Lewes; 5: Southwick Hill 1; 6: Southwick Hill 2; 7: Harrow Hill; 8: Cissbury; 9: Moon's Copse (Contains British Geological Survey materials © NERC 2015)

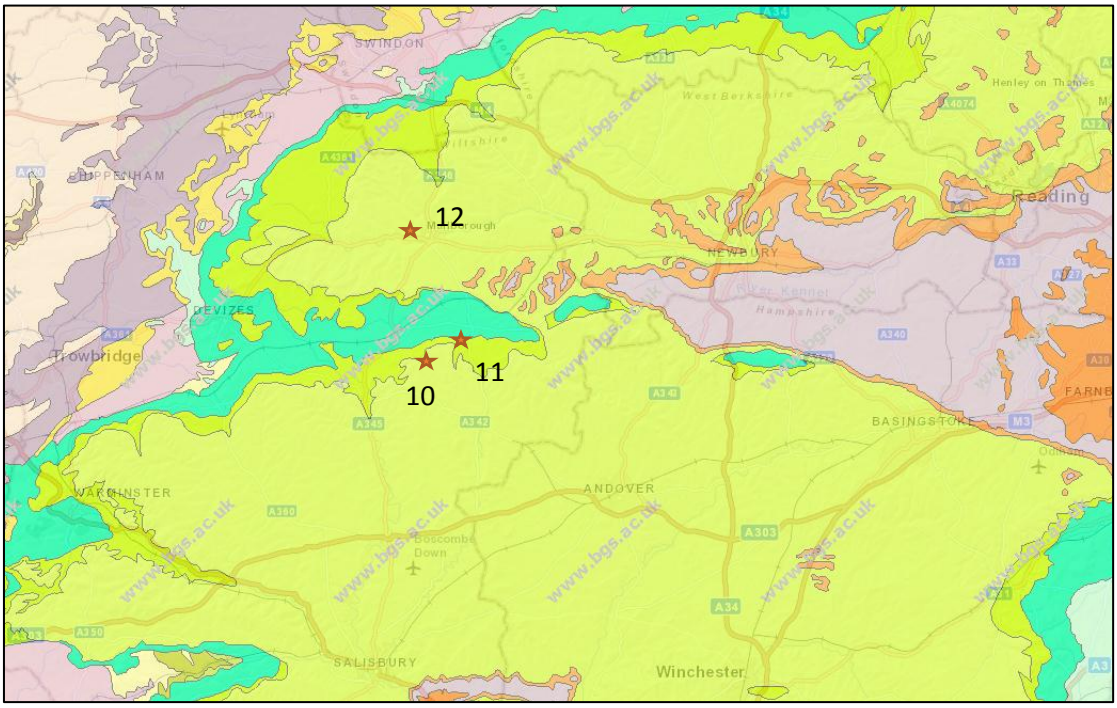


Figure 5.2f – Southern province sampling locations 10: A342 Pewsey; 11: field near Pewsey; 12: West Kennet (Contains British Geological Survey materials © NERC 2015)

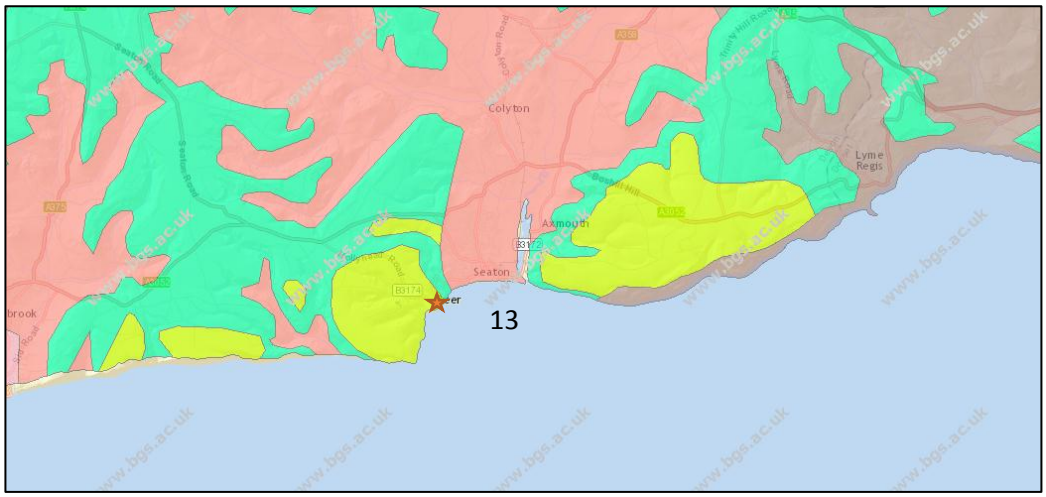


Figure 5.2g – Southern province sampling locations 13: Beer (Contains British Geological Survey materials © NERC 2015)

5.2 Sample Preparation

After collection of samples, in order to accurately identify the number of elements present, and the concentration of those elements, the sample itself must be absolutely free of contamination. Contamination can occur from a number of different sources, at any stage of analysis, therefore great care must be taken when preparing the sample.

During collection, samples of flint were not reduced in the field as they were frequently covered in soil or other potential contaminant. Instead, after collection, the samples were first cleaned, air-dried, and placed in new, unused plastic bags. The preparation of samples for pXRF and ICP-MS varies considerably, however any samples that had large/numerous chalky or fossiliferous inclusions were excluded from both methods of analysis. Chalky inclusions throughout the flint (either an area of chalk formed within the flint, or small 'speckled' areas of very light coloured flint) could provide erroneous results. The chalky cortex on the exterior of nodules or pebbles was also excluded from analysis. Fossil inclusions are common in flint and

are composed of a quartz-like crystalline material that could potentially introduce contamination. These areas were not selected for sampling.

5.2.1 Sample preparation for portable X-Ray fluorescence (pXRF)

The sample preparation for pXRF analysis was relatively straightforward. After washing and air-drying overnight, the flint was reduced (knapped) in the laboratory to obtain a fresh surface for analysis. This surface was inspected to ensure that there were no inclusions that would affect the analysis, and that it was as flat and even in surface topography as possible. The sample was then tested. Some samples were deemed to be unsuitable for analysis due to internal flaws discovered during reduction. The samples that were tested using pXRF are listed below (table 5.2); these samples met the criteria for pXRF analysis outlined above.

Site	**Samples Analysed**
Arras Hill chalk pit	1 (*3*), 2 (*3*), 3 (*3*)
Ballintoy	1 (*3*), 2 (*7*)
Beer	1 (*10*), 2 (*7*)
Cissbury	1 (*5*), 2 (*7*)
Cloughastucan	1 (*1*), 2 (*1*)
Dover, Coast	1 (*4*), 2 (*1*), 3 (*2*), 4 (*2*), 5 (*3*)
Field near Pewsey	1 (*5*), 2 (*6*)
Garron Point	1 (*1*), 2 (*1*)
Grime's Graves	1 (*9*), 2 (*4*)
Harrow Hill	1 (*4*), 2 (*3*)
Isle of Wight Lane	1 (*4*)
Kingston, Lewes	1 (*11*)
Malton	1 (*1*), 2 (*2*)
Middleton Quarry	1 (*3*), 2 (*3*)
Mill Hill	1 (*3*), 2 (*2*)
Moon's Copse	1 (*3*), 2 (*3*)

North Landing	1 (*2*), 2 (*2*), 3 (*1*), 4 (*1*), 5 (*1*), 6 (*2*), 7 (*2*), 8 (*2*), 9 (*1*), 10 (*2*), 11 (*2*), 12 (*1*), 13 (*1*), 14 (*1*), 15 (*1*),16 (*1*), 17 (*2*), 18 (*2*)
North Ormsby	1 (*3*), 2 (*3*), 3 (*3*), 4 (*3*)
Portbraddan	1 (*7*), 2 (*3*), 3 (*6*), 4 (*4*)
Rifle Butts Quarry	1 (*3*), 2 (*3*), 3 (*3*)
Sledmere/Malton	1 (*3*), 2 (*3*)
Slieve Gallion	1 (*5*), 2 (*6*), 3 (*6*)
Southwick Hill	1 (*12*), 2 (*3*)
Welton-le-Wold	1 (*3*)
West Kennet	1 (*1*), 2 (*2*)
White Park Bay	1 (*4*), 2 (*9*), 3 (*4*), 4 (*5*), 5 (*8*)
White Rocks	1 (*4*), A1 (*4*), A2 (*2*), B1 (*3*), B2 (*2*), 3 (*3*), 4 (*2*), 5 (*10*), 6 (*4*), 10 (*5*)

Table 5.2 - pXRF samples (number of analyses per sample indicated by italicised figure in parentheses)

5.2.2 Sample preparation for inductively coupled plasma-mass spectrometry (ICP-MS)

Sample preparation for ICP-MS is more complex and time-consuming. Flint samples were chosen based on the criteria outlined above for pXRF samples (section 5.2.1). The sample, after being washed and dried, was reduced into much smaller fragments (less than 10mm in size). Small pieces of flint that were free from inclusions and cortex were selected for analysis. These fragments were ground into a fine powder using a mechanical ball mill (courtesy of the Department of Archaeological Sciences, University of Bradford). This ball mill used a hardened steel crucible and ball which vibrate to crush any sample placed within the crucible. It was necessary to use small fragments of flint as the ball mill had difficulty breaking up larger samples. The samples of flint were placed in the machine for approximately 3-3.5 minutes. The

resulting powder was very fine in texture. The powder from each sample was weighed and placed into clean test tubes, then labelled. The ball mill was thoroughly cleaned beforehand, and between each sample to prevent contamination with analytical grade acetone (99.5+ %) – this stage increased the time spent using the ball mill but was absolutely necessary to ensure that no contamination was introduced. Each sample was a fine powder and ready for digestion and analysis.

Site	Samples Analysed
A2 Dover	1 (*1*), 2 (*1*)
A342, Pewsey	1 (*2*)
Ballintoy	1 (*3*), 2 (*3*)
Beer	1 (*1*), 2 (*1*)
Carnlough	1 (*3*), 2 (*3*), 4 (*3*), 5 (*1*), 7 (*2*), 9 (*2*)
Cissbury	1 (*2*), 2 (*3*)
Cloghastucan	1 (*2*), 2 (*3*)
Coast, Dover	1 (*2*), 2 (*2*)
Field near Pewsey	1 (*1*), 2 (*1*)
Garron Point	1 (*2*), 2 (*2*)
Grime's Graves	1 (*1*)
Hackpen Hill	1 (*1*), 2 (*1*)
Harrow Hill	1 (*1*)
Isle of Wight Lane	1 (*1*)
Landpark Wood	1 (*3*)
Moon's Copse	4 (*2*)
Murlough Bay	1 (*1*)
Portbraddan	1 (*1*), 2 (*2*)
Slieve Gallion	1 (*3*), 2 (*5*), 4 (*1*), 6 (*2*)
Southwick Hill	1 (*4*), 2 (*2*)
White Park Bay	1 (*3*), 2 (*2*), 3 (*1*), 4 (*1*), 5 (*1*)
White Rocks	1 (*1*), 3 (*3*), 4 (*3*), A1 (*2*), A2 (*1*), B1 (*3*), B2 (*2*)

Table 5.3 ICP-MS samples (number of analyses per sample indicated by italicised figure in parentheses)

5.3 Analysis

Investigation of the flint samples was undertaken using two different analytical methods. Each of these methods has inherent benefits to this kind of analysis. Portable X-ray fluorescence is a non-destructive, quick, and comparatively cheap approach that can be used in the field. ICP-MS is a destructive method that requires greater time investment and specialised equipment; however it can detect a wider range of elements, and at lower concentrations. Prior to analysis, risk assessments and COSHH forms were completed and approved by the relevant staff.

5.3.1 pXRF

The washed and dried flint samples were reduced in the lab to obtain a fresh surface for analysis. The surface, free of chalky and/or fossiliferous inclusions, must also be as flat as possible to reduce scattering of the X-rays generated by the XRF spectrometer. The instrument used in this study is a Bruker Tracer III handheld XRF spectrometer. The sample was placed on the test stand as close as possible to the X-ray aperture to minimise scattering. A number of samples were placed within a test case, with the spectrometer secured underneath, as they were too large to use on the test stand.

Using the accompanying software, the spectrometer was set to 40kV, 15μA, with no filter applied. The sample was analysed for 60 seconds under these settings. Due to variation within each flint nodule in terms of inclusions, some samples were analysed less frequently than others; table 5.2 outlines how many readings were taken from each sample. This amounted to approximately 5-10 minutes of time spent analysing each sample, including turnaround for the next flint sample and selecting area for analysis. As pXRF analysis has not previously been conducted on flint from Britain or Ireland, a wide range of elements were analysed. The pXRF

spectrometer can only detect elements within a specific range, in this instance elements between magnesium and uranium can be detected. The elements chosen for this study were: magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, rubidium, strontium, yttrium, zirconium, niobium, molybdenum, caesium, lanthanum, cerium, praseodymium, ytterbium, lutetium, lead, thorium, and uranium. Rhodium and barium were detected also, however the pXRF spectrometer hardware contains both these elements, and the results obtained may in fact represent false readings so they were excluded from analysis. The readings for palladium were comparatively high compared to the other elements detected during the pXRF analysis. Palladium can occur in geological contexts in soluble mineral grains or be embedded in silicate minerals; it is also the element with the lowest abundance in the earth's crust (Godlewska-Żyłkiewicz & Leśniewska 2006, 101). However the pXRF spectrometer used for this analysis (Bruker Tracer III handheld pXRF spectrometer) contains palladium components and will therefore introduce interference and erroneous results. Detection of palladium in flint samples was therefore due to instrumental interference and not an actual reading, given palladium's extremely low abundance in the earth's crust.

5.3.2 ICP-MS

Prior to ICP-MS analysis, the sample was digested in nitric acid to form a solution. The acid digestion took place in a microwave where the samples were sealed in vessels with nitric acid. The microwave used in this study was a CEM MARS 5 (microwave accelerated reaction system) oven. As any contamination would lead to inaccurate results, the microwave vessels were rinsed with deionised water prior to use. When completely dry, the vessel caps were inspected and the plastic rupture disc was replaced. The plastic rupture disc is a failsafe measure to prevent the vessel exploding under high pressure, and ensures that digestion occurs under

closed conditions. The sample was weighed out into the clean vessels; 0.04g of each sample was used. Due to the lengthy sample preparation and analysis process, it was not possible to analyse every sample multiple times. The focus was instead on obtaining results from samples from different areas; some areas are therefore represented by small numbers of samples. The numbers of samples and ICP-MS readings per site are outlined in table 5.3.

Concentrated (70%) nitric acid was then added, in this instance 10ml was pipetted into each vessel. The vessel was capped and placed inside a Kevlar sleeve, then clamped inside a support module using a torque wrench. Precise measurement was essential to ensure that the resulting data is accurate.

The vessels were placed on the carousel inside the microwave. One vessel (control vessel) had a small opening to permit the introduction of a fibre optic temperature sensor. This sensor was secured at the top of the microwave interior with a snap-in port, and the temperature-sensitive end was inserted into the vessel, ensuring that it reached the sample mixture at the bottom of the vessel. Although the microwave has slots for 12 vessels, due to equipment limitations a maximum of eight vessels could be placed within the microwave at any time. This increased the time taken for the digestion stage as the microwave could not be used to its full potential.

The microwave was programmed to monitor the digestion process. For this study, the microwave was programmed to heat the samples to 200°C, ramping to this temperature over 15 minutes. The temperature was then maintained for 60 minutes, and then cooled over a period of 120-180 minutes, or until the temperature measured by the sensor was less than 50°C. If the vessels were opened prior to this, the sudden release of pressure would lead to loss of samples and potential injury. The vessels were opened within a fume cupboard as nitric

acid vapour was released when the cap was removed. Inhalation of this vapour can have serious health consequences. In total, the time spent cleaning vessels, weighing samples, preparing for digestion, and the necessary cool down, resulted in approximately five hours spent digesting eight samples.

The finely ground flint was fully digested and no particulates were visible within the solution. The samples were now prepared for introduction to the ICP-MS. 100 µl of sample solution was pipetted into a 10ml test tube, this was topped up to 10ml with 9900 µl deionised water. The test tubes were placed on the autosampler. The ICP-MS was controlled through the accompanying software, PlasmaLab. The programme selected for this study conducts a sweep that will identify and quantify a large range of elements: lithium, beryllium, sodium, magnesium, aluminium, potassium, calcium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, rubidium, strontium, molybdenum, cadmium, caesium, barium, and lead. ICP-MS can identify a larger range of elements than pXRF, and at lower concentrations.

Analysis included an external standard, SIGMA-ALDRICH 54704 multielement standard solution 5 for ICP (in 10% nitric acid). The elements that were present in this standard in certified quantities were: argon, aluminium, barium, beryllium, bismuth, calcium, cadmium, cobalt, chromium, caesium, copper, iron, gallium, indium, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, lead, rubidium, strontium, thallium, vanadium, and zinc. The standard solution was run at seven different concentrations: 0.5ppb (parts per billion), 1ppb, 1.5ppb, 2ppb, 2.5ppb, 4ppb and 5ppb.

5.4 Analysis of results

5.4.1 pXRF results

The pXRF results were gathered by the accompanying software, S1PXRF (figure 5.3), which generates a spectrum of results. Further analysis was undertaken by ARTAX, software that identifies the elements that have been detected and determine the number of counts per second gathered for each identified element. For each pXRF reading, elements must be identified and data imported to Excel manually. Counts per second were calculated from the net area underneath each elemental peak on the spectra. The counts per second were collated in an Excel spreadsheet to facilitate analysis. The pXRF results were converted into relative percentages and differences between elements readings from sites were investigated for statistical significance using unpaired t-tests using the Data Analysis feature embedded in Excel (figure 5.4). For the purposes of this study a *p* value of less than 0.05 was considered to be statistically significant.

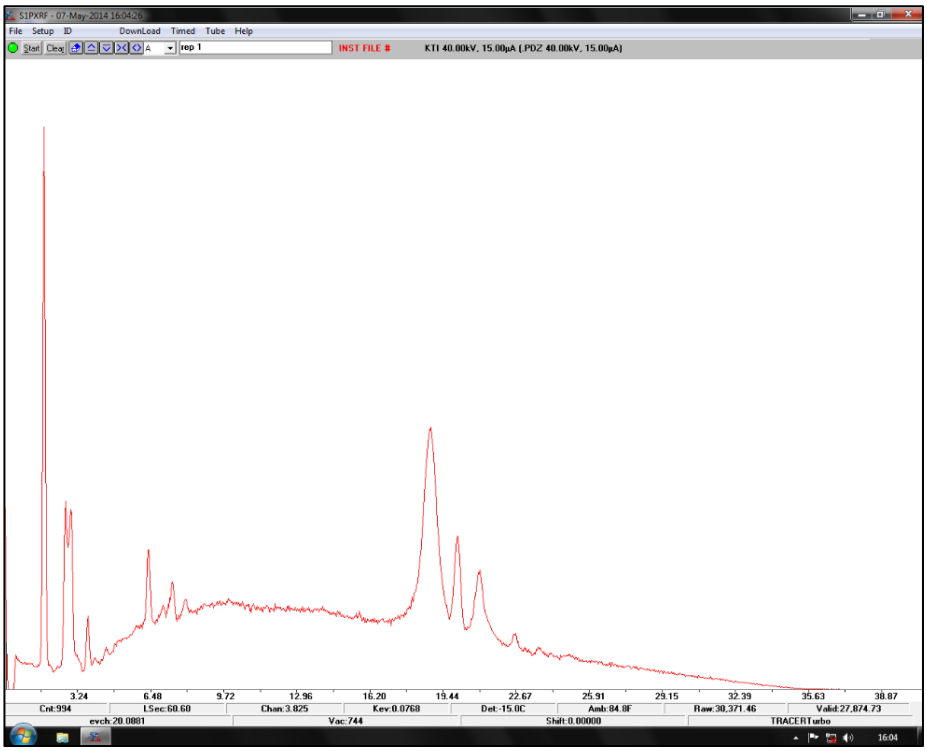


Figure 5.3 – pXRF spectra shown in S1PXRF

t-Test: Two-Sample Assuming Unequal Variances		
PHOSPHORUS		
	Variable 1	*Variable 2*
Mean	0.002391337	0.000959108
Variance	1.84473E-06	1.54854E-06
Observations	25	29
Hypothesized Mean Difference	0	
df	49	
t Stat	4.015967525	
P(T<=t) one-tail	0.000101451	
t Critical one-tail	1.676550893	
P(T<=t) two-tail	0.000202903	
t Critical two-tail	2.009575237	

Table 5.4 – Example of t-test result

This study represents a preliminary investigation of the geochemical variability of flint within Britain and Ireland. The results from this analysis will provide an indication of the feasibility of provenancing flint using pXRF. Subsequent investigations of flint from Britain and Ireland may wish to include and/or compare the results obtained here, however comparing the pXRF results acquired here to results from other studies will rely on a number of factors.

Inter-laboratory reproducibility is a pressing issue in the field of pXRF as the widespread introduction and low cost of handheld pXRF spectrometers, in addition to the 'user friendly' operation of the device, has led to a proliferation of studies on particular materials (Heginbotham *et. al.* 2010, 244). However issues arise when comparing data collected as part of separate studies, or on different instruments. This has been countered by calibrating the spectrometer through the utilisation of internationally-recognised reference standards – these are materials that contain known quantities of particular elements which are analysed alongside the samples under investigation and which should be widely available. Reference standards can be analysed by multiple different instruments and can be used to compare results from different laboratories. Calibration can be achieved using empirical calibration (reference standards), or through fundamental parameters calibration or standard-less calibration; fundamental parameters calibration and standard-less calibration have attracted some degree of controversy due to validity and reliability concerns (Towett *et. al.* 2015, 119). Additionally, not all XRF instruments can implement fundamental parameter correction algorithms (Frahm 2014, 108).

The pXRF results presented in this thesis have not been calibrated; instead the results have been expressed as relative percentages of the net count for each element. Comparison of results between different laboratories or researchers can be impossible if results are reported in machine-specific units rather than internationally recognised standard units such as parts

per million (ppm) (Hughes 1998, 108). In light of this, the results outlined here in relative percentages can be compared to results obtained elsewhere under the same instrumental conditions.

However in order for the results outlined here to be compared to those obtained in future research, the analyses would have to be conducted under the same operational parameters and include the use of internationally available reference standards to fully quantify the results.

5.4.2 ICP-MS results

The results of the ICP-MS analysis were collected by the accompanying software, PlasmaLab, which converted results into Excel spreadsheets (figure 5.4).

	6207/08/2015 11:59:11						
User Pre-dilution: 1.000							
Run	**Time**	**7Li**	**9Be**	**23Na**	**24Mg**	**27Al**	**39K**
		ppb	**ppb**	**ppb**	**ppb**	**ppb**	**ppb**
1	11:59:29	-0.009	0	1.011	0.259	1.64	-0.151
2	11:59:47	-0.003	0.002	1.062	0.268	1.661	-0.066
3	12:00:04	-0.003	-0.001	1.126	0.265	1.675	0.036
x		-0.005	0	1.066	0.264	1.658	-0.061
		0.003	0.002	0.058	0.005	0.017	0.094
%RSD		68.03	312.2	5.413	1.791	1.054	154.2

Figure 5.4 – Excerpt of ICP-MS results from sample 62

The samples for ICP-MS were calibrated to an external standard and therefore were provided in concentrations of parts per billion (ppb). The results in ppb were collated in Microsoft Excel

and analysed using unpaired t-tests to investigate statistical significance. As with the pXRF results, a *p* value of less than 0.05 was considered to be statistically significant.

5.5 Blind provenance testing

5.5.1 Discriminant function analysis

The results of the artefact assemblage pXRF and blind provenancing pXRF and ICP-MS studies were subjected to discriminant function analysis (undertaken using SPSS (Statistical Software for the Social Sciences) v. 20). Discriminant function analysis is a multivariate statistical technique that determines which variables distinguish between two or more groups, and enables the classification of unknown objects into those groups. The groups are established prior to analysis and unclassified samples/observations are assigned group membership based on the measured variables.

In this study, the previously defined groups were the areas of flint occurrence in Britain and Ireland: Northern Ireland, Northern, Southern, and Transitional. The variables used to differentiate between these groups were the elements detected during analysis of the flint samples. Discriminant function analysis in this study highlighted which elements best discriminate between the areas of Britain and Ireland where flint occurs.

Discriminant function analysis was selected for this study as it can reveal which variables (elements) maximally separate the groups and which variables are least useful. This will inform future provenancing studies and provide a more discrete group of elements for particular focus. Most importantly, discriminant function analysis facilitates the classification of new samples into the groups that have been established; this was vital to determine the source of archaeological artefacts, fulfilling one of the major objectives of this research.

A drawback of this approach was that the discriminant function analysis classifies samples to the groups to which they are most similar, these groups are determined before analysis and does not allow for a sample which originates from a different group. For example, groups A, B, and C are determined before discriminant analysis, however a flint sample from group D would not appear as an outlier, but would be classified to A, B, or C depending on what group it matched most closely to.

5.5.2 pXRF blind provenancing

In order to test the strength of the pXRF provenancing, 18 samples were selected for blind provenance testing and compared with 273 results from flint samples collected from locations within the study area. Blind samples were chosen and anonymised by Dr. Vicki Cummings, who picked a random selection from the study area. These samples were analysed following the methodology outlined in 5.3.1 and 5.4.1. In essence, these samples represent a hypothetical assemblage of raw material, the origins of which are unknown. Discriminant function analysis was conducted to determine if these samples can be accurately provenanced to their source areas, and whether non-local samples can be differentiated.

5.5.3 ICP-MS blind provenancing

In order to provide a comparison with the pXRF blind provenancing tests, a similar analysis was conducted with the results from the ICP-MS samples. Due to the time-consuming and destructive nature of the acid-digestion process, a random selection of ICP-MS results were inserted into the discriminant function analysis as ungrouped cases to mimic an artefactual assemblage, as opposed to removing a sample from the artefacts themselves.

There are 126 ICP-MS samples from the study area as a whole. Half of these were selected at random to be the blind provenancing assemblage. The random selection was conducted in Microsoft Excel, using the RANDBETWEEN formula, which, when inserted into a cell as "=RANDBETWEEN(1,126)", provides a random number between 1 and 126. Copied and pasted into 63 cells, this formula provided the samples numbers for the blind provenancing analysis. There was no consideration taken to ensure a representative group drawn from all of the potential sample locations within the study area, the aim was to be as indiscriminate as possible. This group was then subject to discriminant function analysis. The following chapters outline the results obtained from the pXRF and ICP-MS analyses.

5.6 Replicated pXRF analysis

Assessing the geochemical variability of the raw material was accomplished by running multiple analyses on one sample. The analyses were conducted on different areas on the same sample, provided those areas were free of inclusions, patina, or cortex. The pXRF analysis procedure as outlined above was conducted repeatedly on a sample collected from Slieve Gallion (table 5.5).

	Slieve Gallion Sample 1					Mean	Standard Deviation	Coefficient of Variation %
	Rep.1	Rep.2	Rep.3	Rep.4	Rep.5			
Si	44240	35441	35069	35514	35400	37132.8	3976.7	10.7
P	122	130	124	135	118	125.8	6.7	5.3
Cl	2383	2457	2754	2256	2434	2456.8	183.4	7.5
K	1179	841	712	951	818	900.2	177.5	19.7
Ca	7002	6344	6578	6433	6620	6595.4	252.9	3.8
Ti	708	623	245	614	323	502.6	204.8	40.7
V	69	87	76	79	66	75.4	8.3	11.0
Mn	1426	1499	1741	1534	1720	1584	139.5	8.8
Fe	18296	16553	16642	16282	16791	16912.8	795.1	4.7
Co	1089	1067	1112	1220	1001	1097.8	79.9	7.3
Ni	5778	5666	5227	6111	5753	5707	317.2	5.6
Cu	2028	1895	1760	2306	2162	2030.2	214.9	10.6
Zn	1236	1189	981	1298	1109	1162.6	122.7	10.6
Rb	66	57	79	87	51	68	15.0	22.0
Sr	1566	1592	1251	1486	1001	1379.2	250.5	18.2
Y	1	4	3	5	2	3	1.6	52.7
Zr	968	1526	1269	1069	917	1149.8	249.8	21.7
Cs	351	313	289	125	243	264.2	87.1	33.0
La	40	76	85	57	61	63.8	17.5	27.4
Ce	202	254	215	225	267	232.6	27.1	11.7
Pr	903	951	963	897	930	928.8	28.9	3.1
Yb	4131	4671	4235	4432	4325	4358.8	206.9	4.7
Lu	235	254	247	275	226	247.4	18.8	7.6
Pb	513	669	940	633	678	686.6	156.2	22.8
Th	168	547	289	335	412	350.2	141.2	40.3
U	547	489	457	462	476	486.2	36.2	7.4

Table 5.5 – results of replicated pXRF analysis on flint sample from Slieve Gallion, Northern Ireland

The results in table 5.5 include calculations of the mean, standard deviation, and the coefficient of variation. Standard deviation is an absolute measure of variation and provides an indication of how a group of data is clustered around its mean; generally speaking, a large standard deviation indicates that the group of results are highly variable. However, interpreting standard deviation can be problematic as it depends on the unit in which it was calculated (Weisberg 1992, 57). The coefficient of variation is a relative measure of variation, calculating the amount of variation in a set of measurements as a percentage of the mean of those measurements – e.g. a coefficient of variation of five demonstrates that the average reading within a dataset differs from the mean by five percent of the value of the mean (Hanneman *et. al.* 2012, 135). Coefficient of variation is a useful measure of variability where there are multiple groups of data, each with different mean values, as it permits the evaluation of the variation relative to what is typical for that group (*ibid.*).

The results in table 5.5 show that there are some elements (such as silica and iron) that have larger standard deviations, i.e. the results are widely dispersed. However there are some elements where the standard deviation is low (ytterbium, phosphorus), indicating that the results are tightly clustered around the mean. The coefficient of variation for both silica and iron are comparatively small, suggesting low variability in the measurements of these elements.

Table 5.6 below outlines the results of repeated analyses of a sample from Harrow Hill (located in the Southern Chalk province). The elements with the highest standard deviation are silica and iron, as was found with the results from Slieve Gallion (table 5.5).

	Harrow Hill Sample 1					Mean	Standard Deviation	Coefficient of Variation %
	Rep.1	Rep.2	Rep.3	Rep.4	Rep.5			
Si	76991	73014	80553	74005	88446	78601.8	6238.3	7.9
P	2495	2442	2498	2497	2311	2448.6	80.5	3.3
Cl	2549	3070	2818	2985	3021	2888.6	212.2	7.3
K	2586	2730	2740	3014	3111	2836.2	218.1	7.7
Ca	7698	6087	9890	6644	12782	8620.2	2743.4	31.8
Ti	1874	1757	1815	1813	2146	1881.0	153.8	8.2
V	1	1	1	1	1	1.0	0.0	0.0
Mn	1367	1346	1528	1131	1402	1354.8	143.6	10.6
Fe	3987	4484	4845	5428	5807	4910.2	726.4	14.8
Co	1137	671	1139	1293	1777	1203.4	396.6	33.0
Ni	1106	751	989	1154	1451	1090.2	254.9	23.4
Cu	2739	2408	2630	3053	2775	2721.0	234.4	8.6
Zn	579	359	478	436	313	433.0	104.0	24.0
Rb	271	293	395	154	1	222.8	150.7	67.6
Sr	1425	1279	1878	1136	1630	1469.6	292.5	19.9
Y	88	199	356	460	772	375.0	263.9	70.4
Zr	5953	6238	6551	6323	6377	6288.4	219.7	3.5
Cs	410	272	99	184	420	277.0	140.1	50.6
La	241	153	97	1	140	126.4	87.5	69.2
Ce	326	248	194	247	250	253.0	47.1	18.6
Pr	980	1235	984	756	795	950.0	190.4	20.0
Yb	5036	4307	4553	4709	4539	4628.8	269.1	5.8
Lu	306	-1	279	11	48	128.6	151.0	117.4
Pb	851	422	571	468	997	661.8	250.7	37.9
Th	353	320	111	183	142	221.8	108.4	48.9
U	615	319	491	609	345	475.8	140.6	29.5

Table 5.6 - Results of replicated pXRF analysis on flint sample from Harrow Hill, southern England

6.0 PORTABLE X-RAY FLUORESCENCE RESULTS

This chapter will outline the results of the portable x-ray fluorescence (pXRF) analysis. This analysis was undertaken using the methodology as described in Chapter 5. The results of the pXRF analysis are available in Appendix 6.1. Only the elements which differ in a statistically significant manner will be outlined here, full details of statistical analysis are presented in Appendix 6.2. This chapter will detail the results of the pXRF analysis in relation to the research questions previously established.

The pXRF spectrometer data was analysed using ARTAX software, which calculated the net area underneath each elemental peak and converts this into net counts per element. The pXRF results presented here are relative percentages of the elements detected, not absolute concentrations. The pXRF spectrometer can only detect a specific range of elements (magnesium to uranium), so elements that are heavier or lighter in atomic mass are discounted from analysis. Differences in the relative percentages of the elements detected will be investigated for statistical significance. This chapter describes the effect of patina on geochemical provenancing, before moving onto consideration of each of the source areas of flint within Britain and Ireland.

6.1 Effects of patina on geochemical provenancing

Patina is a general term used to describe the change in colour that occurs when flint is chemically weathered (Glauberman & Thorson 2012, 21). Flint can attain a number of different kinds of patina based on its exposure to different environments, such as rain or seawater, or through absorption of chemicals from the depositional context (Luedtke 1992, 99-100). When flint is weathered and/or deposited, silica is leached from the surface forming microscopic cavities – these cavities are then refilled by elements from the depositional context, changing its colour and texture (Graetsch & Grünberg 2012, 22). Patina can vary in colour and texture, ranging from a 'bleached' white appearance to shades of orange or brown. As patina is a result of chemical change in the flint, it has the potential to interfere with provenancing. An analysis of Scandinavian flint using energy-dispersive XRF demonstrated that areas of patina showed depleted levels of silicon dioxide, and elevated concentrations of aluminium oxide, potassium oxide, and especially iron, however calcium oxide concentrations were not significantly greater (Högberg *et. al.* 2012, 230).

No studies currently exist that investigate the effects of patina on provenancing flint from Britain and Ireland, therefore patinated samples collected were analysed to determine what effect this could have on provenancing. This is particularly significant in terms of analysing archaeological artefacts, many of which have patinated surfaces. Twelve samples (from seven sites) were analysed to determine the effects of patina on geochemical analysis: Cissbury, Harrow Hill (four samples), Southwick Hill, Dover coast (two samples), West Kennet, White Park Bay, and White Rocks. These samples represent four different areas of chalk geology: South Downs, North Downs (Dover coast); Salisbury Plain chalk downs (West Kennet); and the Northern Ireland chalk formations (White Park Bay and White Rocks).

It was not known if patination would have a detrimental effect, and if so, if this was the same across different areas of chalk geology, and what variation exists within each of these areas.

6.1.1 South Downs

Two sites in the South Downs were sampled to investigate the effect of patination: Harrow Hill, and Southwick Hill.

Flint samples with patina from Harrow Hill were analysed. The predominant colour of the flint is grey, with a paler grey patina on the exterior surf-ace. Nine elements were recorded from the Harrow Hill samples: silicon, calcium, iron, cobalt, nickel, copper, strontium, zirconium, and ytterbium.

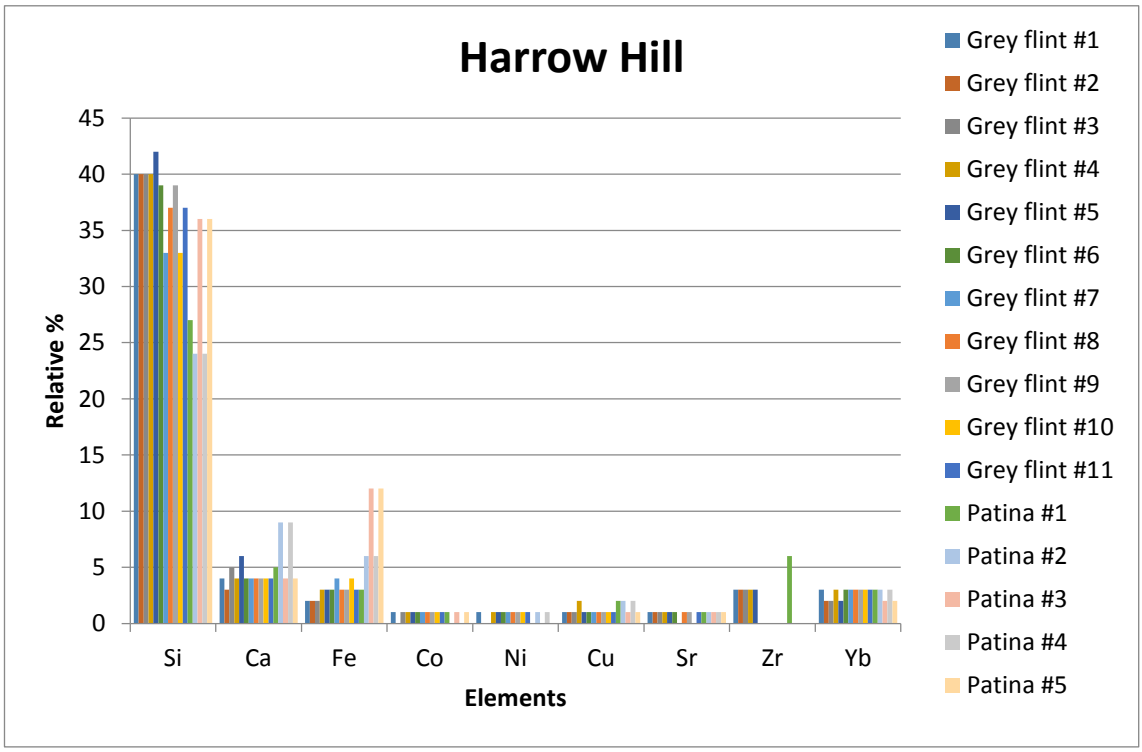


Figure 6.1 – Relative percentages of elements detected in Harrow Hill flint samples, unpatinated vs. patinated flint

Figure 6.1 displays the variation in elements between patinated and unpatinated flint from Harrow Hill, and shows that there is little variation in most of the detectable elements. However, the reading from the patinated surface indicates that silicon levels are depleted and

shows higher readings of zirconium. The results demonstrate that the recorded levels of three elements, silicon (p=0.015), copper (p=0.038), and ytterbium (p=0.015) differ significantly between patinated and unpatinated flint. Despite the apparent differences in the levels of other elements, they do not differ in a statistically significant way.

The sample analysed from Southwick Hill is a large nodule which was reduced to provide clean surfaces. The patina on this flint varies in colour, from white to dark grey, whereas the flint itself is light grey. This nodule contained numerous fossiliferous inclusions which were avoided during analysis. Twelve readings were taken of the unpatinated surfaces, and two readings were taken of the patina. Seventeen elements occurred at relative percentages useful for analysis: silicon, phosphorus, chlorine, potassium, calcium, titanium, manganese, iron, cobalt, nickel, copper, strontium, zirconium, cerium, praseodymium, ytterbium, and lead.

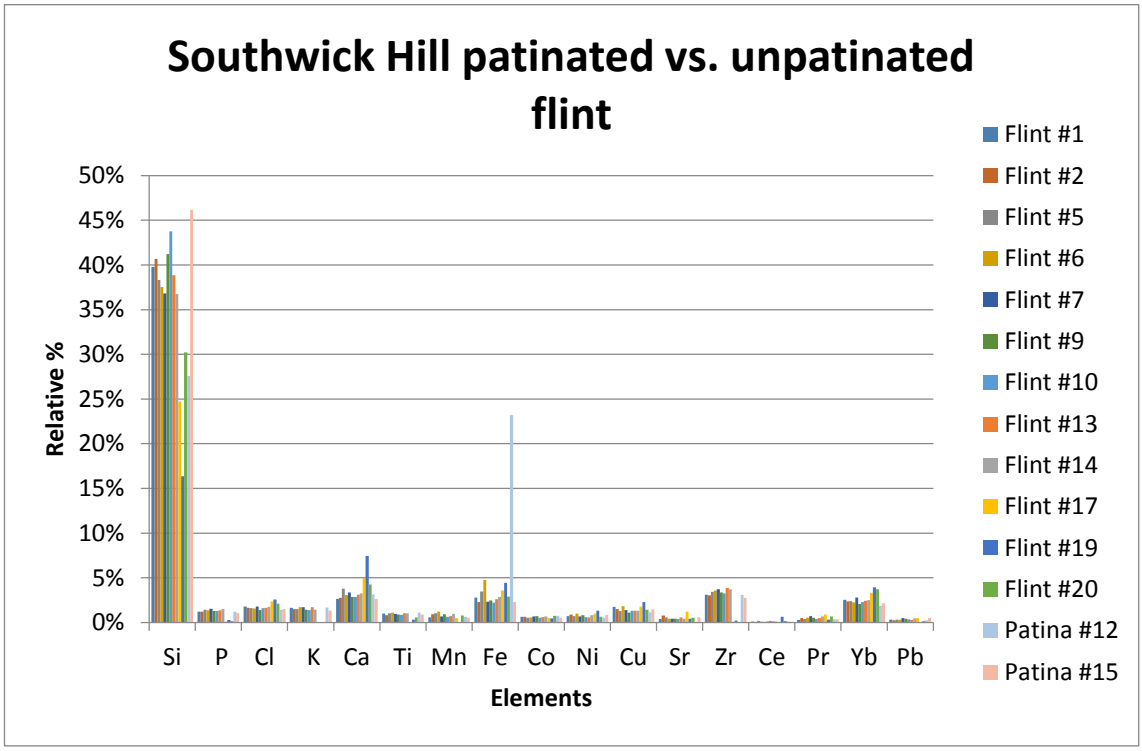


Figure 6.2 – Relative percentages of elements detected in Southwick Hill nodule, unpatinated vs. patinated flint

The white patina was initially assumed to be due to absorption of calcium from the soil, and elevated levels of calcium were anticipated. This was not the case, as illustrated by Figure 6.2. Both the white and dark grey patina do not contain calcium at higher levels than the unpatinated flint. However, the white patina contains over four times as much iron. This was not anticipated as colour changes in flint due to the presence of iron are typically more orange/brown (Cramp & Leivers 2010, 12). White patina is regarded as the result of deposition within sodium- or calcium-rich alkaline soils (Luedtke 1992, 99). The depletion of silicon observed in the patinated surfaces from Harrow Hill is not replicated here. Three elements differ significantly between patinated and unpatinated surfaces: chlorine (p=0.007), praseodymium (p=0.005), and ytterbium (p=0.015).

6.1.2 North Downs

Two samples from the Dover coast were analysed: a large, almost complete nodule, and two smaller nodule fragments. The almost intact nodule was dark grey/brown flint, speckled with small white and orange inclusions. These inclusions would interfere with analysis and were avoided, although they were so prevalent only four readings could be obtained from flint with no inclusions. Five readings were taken on patinated surfaces. This patina is white with orange staining. Fourteen elements were identified in quantities useful for analysis: silicon, phosphorus, chlorine, potassium, calcium, titanium, manganese, iron, cobalt, copper, zirconium, praseodymium, ytterbium, lead.

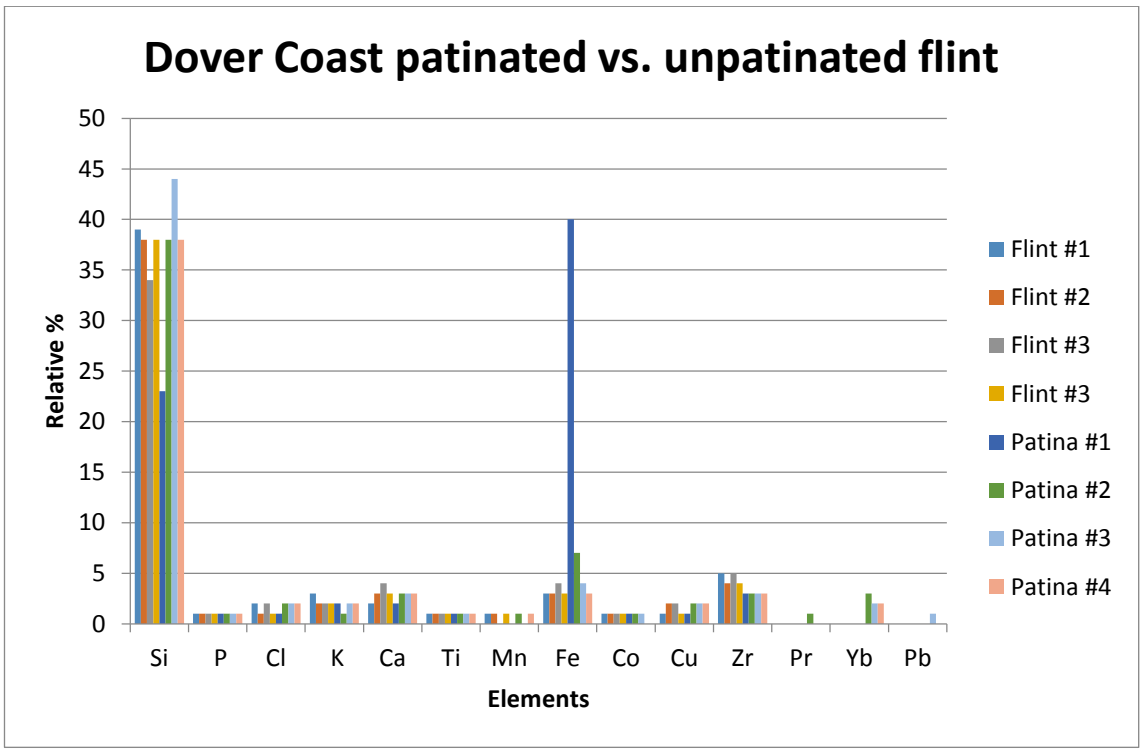


Figure 6.3 – Relative percentages of elements detected in Dover Coast flint, unpatinated vs. patinated flint

It is immediately obvious from Figure 6.3 that one of the patinated surfaces sampled contained higher levels of iron than the unpatinated flint. The high reading from iron could be due to the orange staining on the patina, or could be due to high iron content in the white patina itself, as with the white patina observed on the Southwick Hill nodule. The patinated surface also displays depleted silicon levels, similar to the Harrow Hill nodule patina.

Results demonstrate that the levels of silicon (p=0.012), chlorine (p=0.017), potassium (p=0.035), calcium (p=0.008), copper (p=0.017), zirconium (p=0.009), and ytterbium (p=0.005) differ in a statistically significant way between patinated and unpatinated flint from Dover Coast. None of the other elements display significant differences.

6.1.3 Salisbury Plain Chalk Downs

Two samples were collected from West Kennet, located in Salisbury Plain. The patina on both is a pale grey/white, stained with orange/brown. The unpatinated flint is dark grey. Three readings were taken of the unpatinated flint, and three were taken of the patina. Sixteen elements were identified here: silicon, phosphorus, chlorine, potassium, calcium, titanium, manganese, iron, cobalt, nickel, copper, strontium, zirconium, praseodymium, ytterbium, and lead.

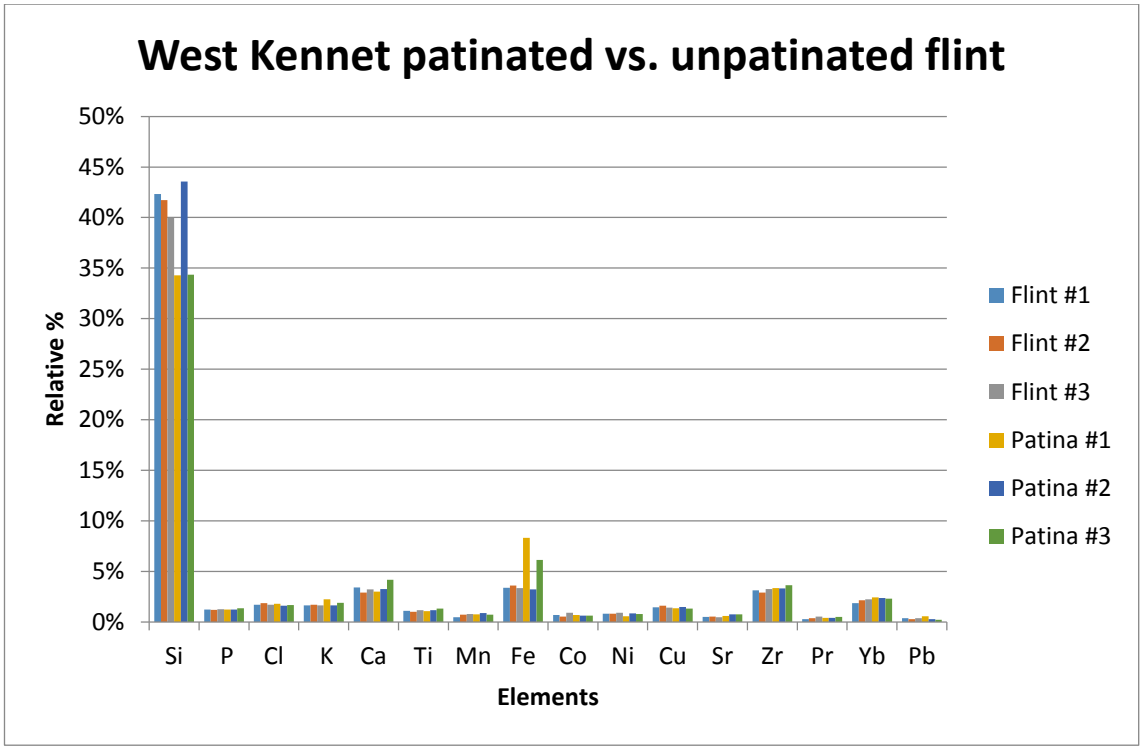


Figure 6.4 – Relative percentages of elements detected in West Kennet fragments, unpatinated vs. patinated flint

Figure 6.4 displays readings from the fragments collected at West Kennet. An area of patina on fragment 1 provided the highest level of iron, along with the lowest level of silicon. Similarly, one of the patina readings on fragment 2 has an elevated level of iron and a reduced level of

silicon. This can be attributed to leaching of silica from the flint in the soil, and subsequent absorption of iron, as demonstrated above in the nodule fragments from the Dover coast. The second pXRF reading of the patinated surface of fragment 2 does not display depleted silicon levels, in fact the level of silicon here is the highest recorded at this site. The iron level is much lower than the other readings from patina. This indicates that the silica has not been leached from this area on fragment 2, and as such there has been no subsequent absorption of iron from the surrounding environment, indicating that the process of patination does not occur at the same rate or across the entire fragment despite appearing to have done so. Despite these differences, none of the recorded elements in patinated and unpatinated surfaces differ in a statistically significant manner.

6.1.4 Northern Ireland chalk formation

Samples from two sites in the Northern Ireland chalk formation are presented here: White Park Bay, and White Rocks. Patinated and unpatinated surfaces from two samples collected from White Park Bay were analysed. The unpatinated flint is dark grey with occasional fossiliferous inclusions. The patinated surfaces are yellow-brown, with inclusions. These inclusions were avoided during analysis. The unpatinated surface on fragment 1 was sampled four times, the patinated surface sampled once. Seven readings were taken of the unpatinated flint on the second fragment, and one reading of the patina. Fourteen elements were identified here: silicon, chlorine, calcium, titanium, manganese, iron, cobalt, nickel, copper, strontium, praseodymium, ytterbium, lead, and uranium.

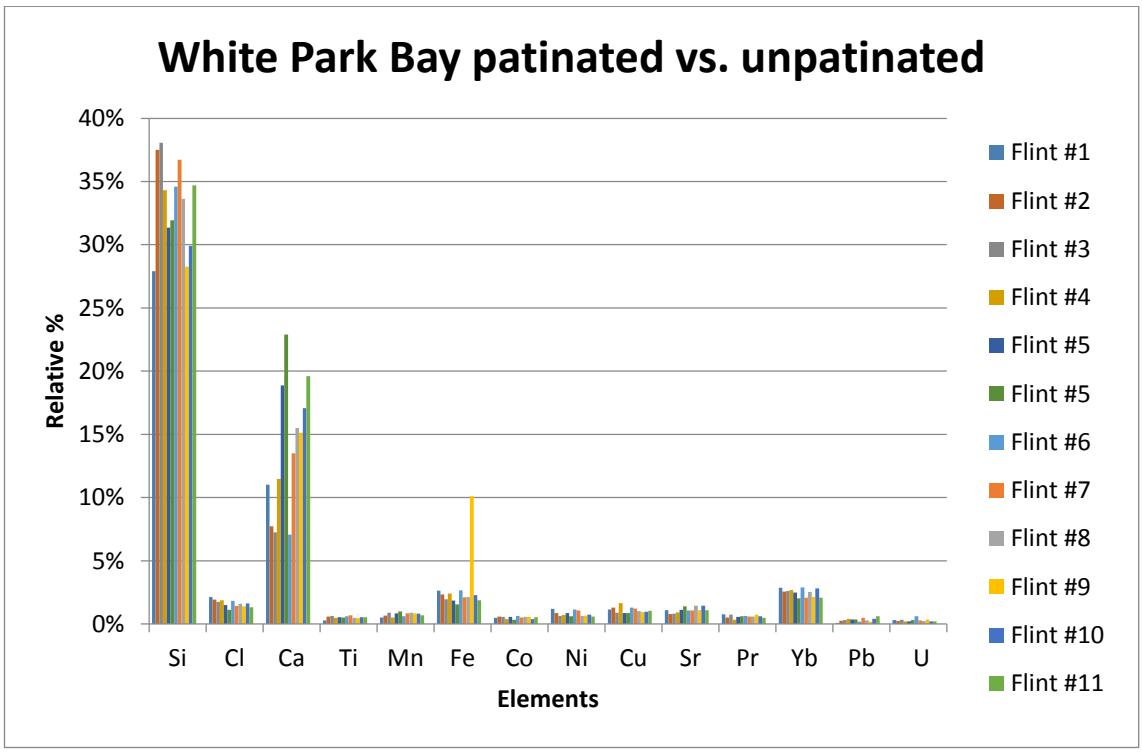


Figure 6.5 – Relative percentages of elements detected in White Park Bay fragment 1, unpatinated vs. patinated flint

The reading from the patinated surface of fragment 1 recorded a lower level of silicon, but elevated levels of both calcium and iron (figure 6.5). As described above, the replacement of silica by calcium and iron occurs during weathering, however in this example calcium levels were elevated in two of the readings taken on unpatinated flint. This indicates that the higher level of calcium in the patina may be a reflection of elevated calcium levels in areas of unpatinated flint.

The patinated surface on the second fragment from White Park Bay also displays depleted silicon levels, as well as elevated iron results. The results recorded for nickel and copper are also slightly elevated. However, a lower level of calcium is recorded here compared to the patina on the first fragment. The higher readings of iron from the patinated surface were

anticipated given the yellow-brown colour of the surface; brown-coloured patina is frequently associated with absorption of iron from the depositional environment (Luedtke 1992, 100), however this is not always the case as the light grey patinated surfaces of the Harrow Hill nodule fragments and the white patina on the Southwick Hill flint both displayed much higher iron levels than the unpatinated surfaces. The differences in the majority of elements recorded on patinated and unpatinated surfaces on the samples from White Park Bay do not differ in a statistically significant way. However, the differences in levels of manganese (p=0.0005), strontium (p=0.006), and ytterbium (p=0.036) are significant.

A large nodule fragment was collected from the beach at White Rocks. The flint varies from light to dark grey and there is a strong orange patina on the exterior surface. Five readings were taken of the unpatinated flint, and four were taken of the patina. Seventeen elements were recorded for these samples: silicon, phosphorus, chlorine, potassium, calcium, titanium, manganese, iron, cobalt, nickel, copper, strontium, yttrium, zirconium, praseodymium, ytterbium, and lead.

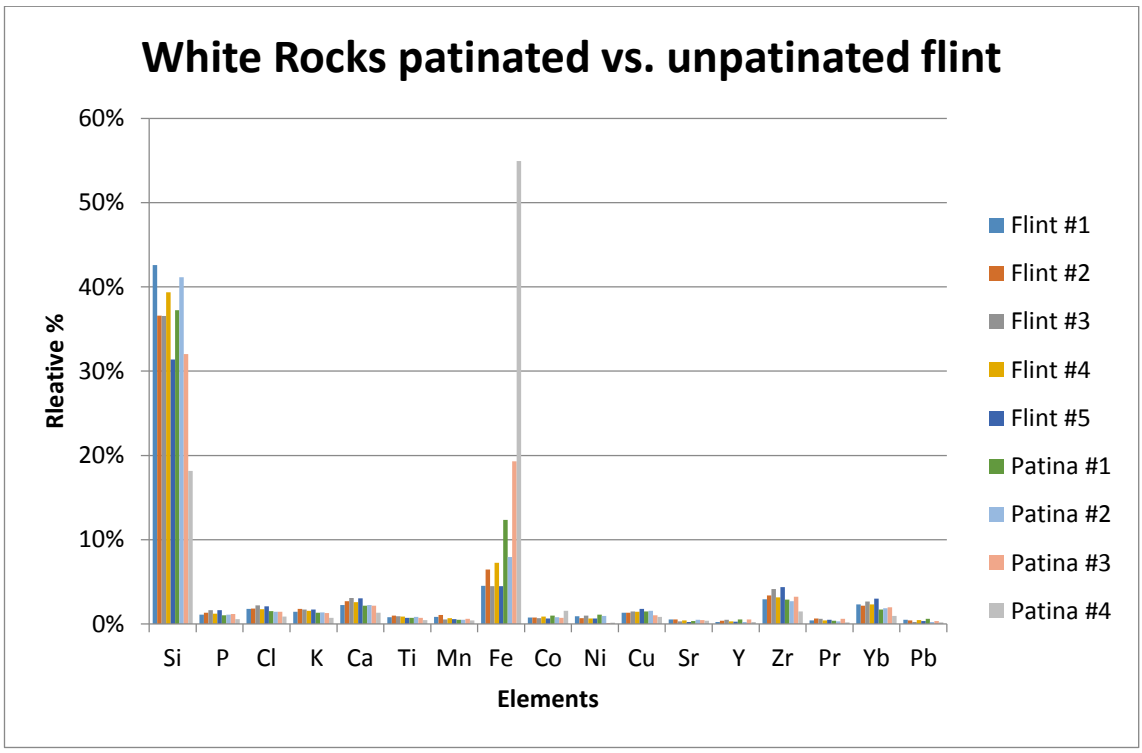


Figure 6.6 – Relative percentages of elements detected in the White Rocks nodule fragment, unpatinated vs. patinated flint

It is immediately clear from Figure 6.6 that the fourth patina reading contains much higher levels of iron than the grey flint, and the other readings from patinated surfaces. This fourth patina reading also displays depleted silicon levels, and no nickel. The calcium levels do not vary between the patinated and unpatinated surfaces, however the levels of silicon and iron do vary. Overall, the levels of iron in the readings from patinated surfaces are higher than those from unpatinated areas; however this is not always matched by depleted silicon levels; the first, second, and third readings from the patinated surface do not show levels of silicon that differ significantly from the readings on unpatinated grey flint.

The small differences observed in the levels of some elements are not statistically significant, and that even the more obvious differences in levels of iron or silicon do not achieve statistical

significance. Chlorine (p=0.018), calcium (p=0.029), and ytterbium (p=0.025) are the only elements whose level differs significantly between patinated and unpatinated surfaces.

6.1.5 Effect of patina on geochemical provenancing

From the figures presented above, it is clear that the presence of a patina can drastically affect the readings obtained from a small number of elements. However the variation in these elements does not occur predictably across different areas of chalk geology. This was anticipated as the formation of a patina is dependent on the minerals in the surrounding soil, which will vary across the study area. The pH of the soil in which the flint has been deposited or weathered will also accelerate or retard the formation of a patina, particularly the alkaline soils of areas of chalk geology (Glauberman & Thorson 2012, 25), such as the chalk downlands found across the south of England. Patinated and unpatinated flint from the South Downs demonstrates significant differences in the recorded levels of silicon, chlorine, copper, praseodymium, and ytterbium; whereas the Salisbury Plain/Pewsey patinated flint samples display no significant differences in the levels of any element compared to unpatinated flint. Samples from the North Downs, however, display significant variation in multiple elements: silicon, chlorine, potassium, calcium, and copper. The flint samples from Northern Ireland displayed significant differences between surfaces with and without patina in terms of levels of ytterbium, chlorine, calcium, strontium, and manganese. The variation of these elements precludes their use for geochemical analysis using pXRF. Patinated surfaces also contain elevated or depleted levels of other elements which may be of use for provenancing. These small variations have the potential to impair attempts at provenancing based on geochemical analysis.

The samples from each geographic area do not display uniformly elevated or depleted levels of the same element, although there appears to be a general trend of patinated surfaces containing high levels of iron and depleted levels of silicon. Possible exceptions to this are the samples from the Northern Ireland chalk formation, which show that elevated levels of iron are always found with depleted levels of silicon. The levels of calcium in patinated surfaces do not appear to vary in the same manner, corroborating the findings of Högberg *et. al.,* who found that the patinated surfaces of Scandinavian flint contain elevated levels of iron and depleted levels of silicon, but calcium levels were unaffected (2012, 230).

6.2 Flint-producing areas within Britain and Ireland

There are four main provinces of flint-producing chalk geology within the study area that will be considered here: Northern, Southern, Transitional, and Northern Ireland. Figure 6.7 displays the extent of the Northern, Southern, Transitional, and Northern Ireland Chalk provinces. The Southwestern province is restricted to the Cretaceous chalk outcrop at Beer, Devon, and has been previously considered as distinct from the rest of the Southern province on the basis of its geochemistry (Bush & Sieveking 1986, 134), although it is a small outcrop, and considered part of the Southern Chalk province by Hopson (2005). This analysis will consider the outcrop at Beer as part of the Southern Chalk province. The provinces described are differentiated on the basis of their lithostratigraphy and faunal content (Hopson 2005, 1), as well as the physical properties of the chalk (Mortimore & Wood 1986, 7).

Geochemical provenancing of archaeological artefacts using pXRF is likely to be impaired by the presence of a patinated surface (see above), however, the removal of patina is not desirous as this will not only have aesthetic repercussions, but would also remove or damage

physical features of the artefact that may be necessary for study. Curators of flint tools may not permit analysis that necessitates removing an area of patina; future analyses of flint artefacts using pXRF are therefore likely to be conducted on patinated surfaces. This section will identify elements useful in distinguishing between chalk provinces in Britain and Ireland, without considering those which have been demonstrated to vary significantly between patinated and unpatinated surfaces. Only elements that do not differ will be considered.

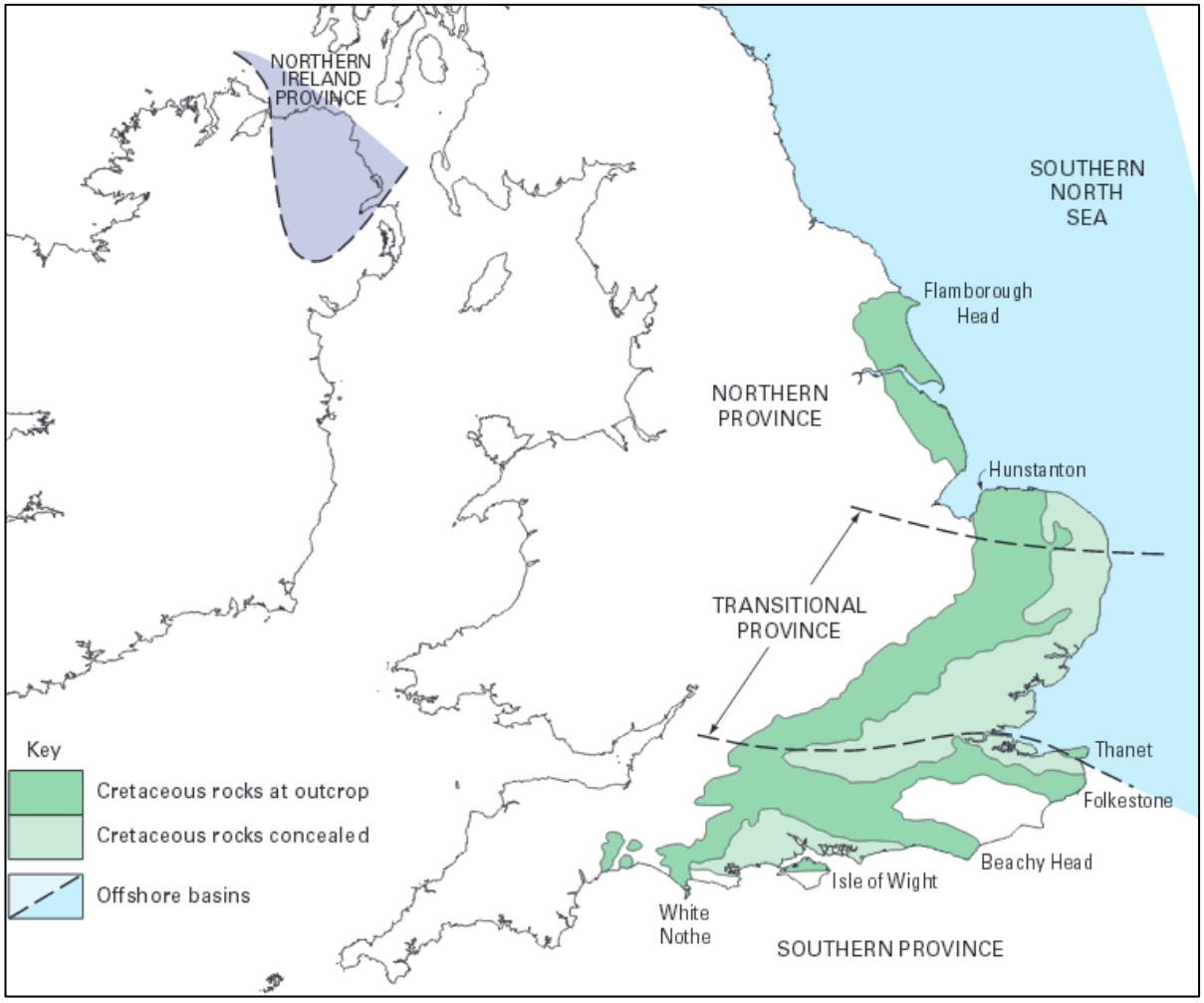


Figure 6.7 – Chalk provinces in England and Northern Ireland (after Hopson 2005, 2)

6.2.1 Northern Chalk province

The Northern Chalk province incorporates the chalk outcrops along the northeastern coast of England, extending from the Wash along the Lincolnshire coast, to the chalk cliffs at Flamborough head in East Yorkshire. The chalk in this province outcrops at the coast, but has also been exposed in modern times through mining activity (e.g. North Ormsby and Arras Hill chalk pits) revealing bands of flint in the process. The Yorkshire and Lincolnshire Wolds are also a source of flint, as they contain deposits of clay-with-flints, the remnants of chalk formations that have been weathered and intermixed with glacial till (Matthews 1976, 231).

Nine sites within the Northern Chalk province were visited and sampled: Arras Hill chalk pit, Malton, Middleton quarry, Rifle Butts quarry, and Sledmere/Malton (East Yorkshire); Mill Hill quarry, North Ormsby chalk pit, and Welton-le-Wold (Lincolnshire); and North Landing (North Yorkshire). The quality of this flint was variable, and some samples provided little or no opportunity for pXRF readings that were free from patina, inclusions, or cortex. It was anticipated that the flint from the coastal outcrops at North Landing could be differentiated from the flint collected from the Wolds of Lincolnshire and Yorkshire. The Wolds flint has been intermixed with clays and soils and it was presumed this would have increased the opportunity for minerals from the clays, soils, and groundwater to be leached into the flint.

From the pXRF analysis of the Northern Chalk province flint fourteen elements were identified: phosphorus, chlorine, potassium, calcium, titanium, chromium, manganese, iron, cobalt, copper, zinc, strontium, cerium, and ytterbium.

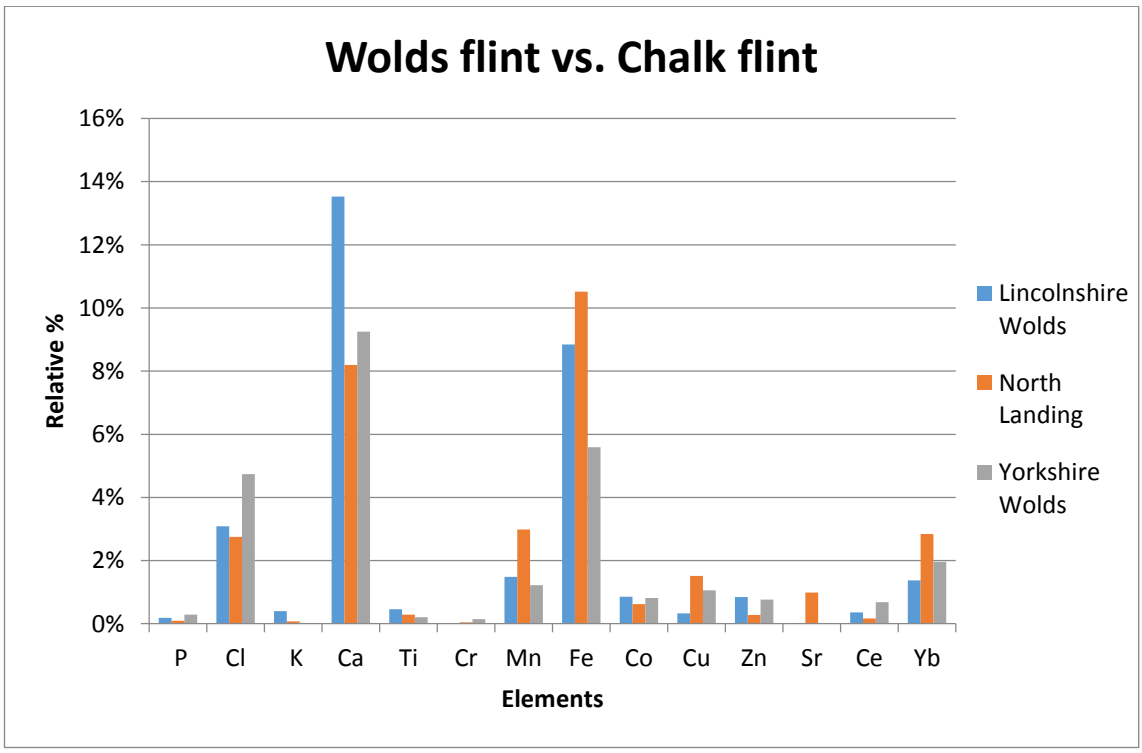


Figure 6.8 – Relative percentages of elements detected in flint from North Landing, Yorkshire Wolds, and Lincolnshire Wolds

Figure 6.8 displays the averaged relative percentages of elements detected in samples from the three main flint-producing areas within the Northern chalk province. These results demonstrate that the flint from the chalk outcrops at North Landing can be discriminated from Wolds flint by significant differences in the levels of phosphorus (p=0.0002), chlorine (p=0.001), iron (p=0.048), cobalt (p=0.0001), copper (p=0.004), and cerium (p=0.0007) detected through pXRF analysis.

Discriminating between the flint from the Yorkshire and Lincolnshire Wolds was also attempted using variations in the levels of fourteen elements (figure 6.9).

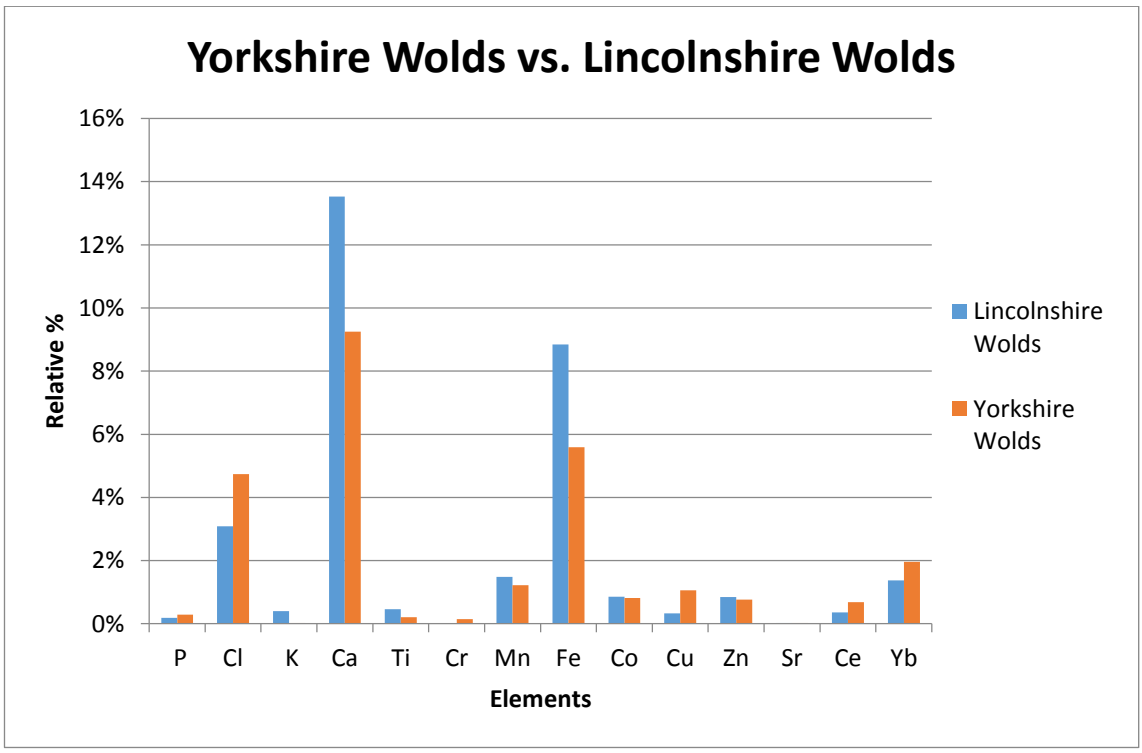


Figure 6.9 – Relative percentages of elements detected in flint from the Yorkshire Wolds and Lincolnshire Wolds

The results indicate that flint from the Yorkshire Wolds and Lincolnshire Wolds can be differentiated through variation in levels of chlorine (p=0.009), potassium (p=0.008), titanium (p=0.043), manganese (p=0.017), cerium (p=0.033), and ytterbium (p=0.023) detected through pXRF analysis.

6.2.2 *Southern Chalk province*

The Southern Chalk province comprises the chalk formation that stretches from Kent to Devon, outcropping at the coast as large chalk cliffs and inland as rolling chalk downlands. The chalk downlands represent the uplift and subsequent erosion of chalk formations above the surrounding geology. If these chalk formations contain flint, the flint can be eroded from the chalk and distributed in the overlying soil. Clay-with-flints formations are frequently found

capping high ground in the chalk downlands in southern England, and are considered to have been an important source of flint during certain periods in prehistory, such as the Mesolithic in the south of England (Care 1982, 279).

Eight sites in the Southern Chalk province provided samples that were suitable for pXRF analysis: Cissbury, Dover coast, a field near Pewsey, Harrow Hill, South Downs Way at Kingston (Lewes), Moon's Copse, Southwick Hill, Beer, and West Kennet. The flint analysed from these locations was highly variable in quality, and readings were taken on areas free of cortex, patina, and inclusions. Within the Southern Chalk province there are several distinct geographic regions: Salisbury Plain/Pewsey (field near Pewsey, Moon's Copse, and West Kennet), South Downs (Kingston (Lewes), Harrow Hill, Cissbury, and Southwick Hill), North Downs (Dover coast), and the Southwestern chalk outcrop in Devon (Beer). As the Southern Chalk province covers a very large area, distinguishing between different regions would aid in more specific provenancing. However, the degree of variation in the elemental composition of the flint within the chalk is unknown, and distinguishing between different regions may not be possible with pXRF. As demonstrated above, samples of patinated and unpatinated flint from the Southern Province displayed statistically significant differences in the recorded levels of seven elements: silicon, copper, ytterbium, chlorine, praseodymium, calcium, and potassium. These elements are not included in the analysis of the Southern Chalk province flint.

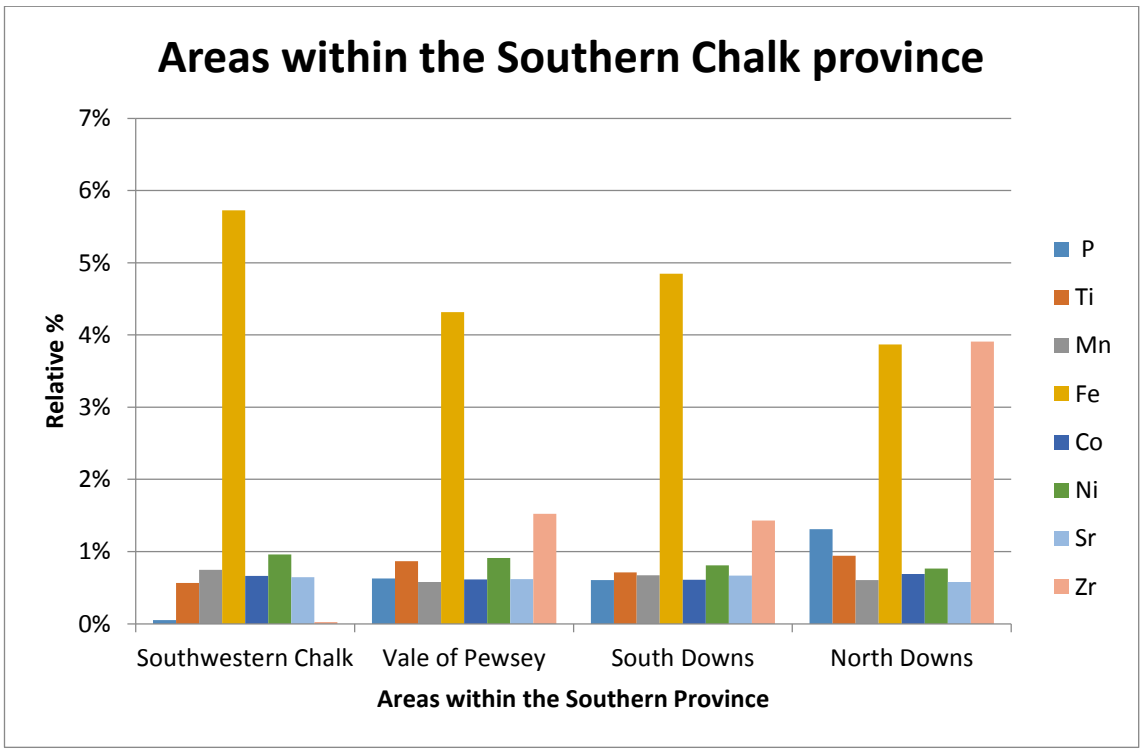


Figure 6.10 – comparison of areas within the Southern Chalk province

From the pXRF analysis of the Southern Chalk province flint eight elements were identified: phosphorus, titanium, manganese, iron, cobalt, nickel, strontium, and zirconium. These elements were used to attempt differentiation between the regions within the Southern Chalk province. Figure 6.10 illustrates the average readings for each of the four areas within the Southern Chalk province. There are some clear differences between the relative percentages of certain elements, particularly zirconium, which is absent in the Southwestern chalk flint and as abundant as iron in the samples from the North Downs. Phosphorus is also more abundant in the North Downs samples compared to the Vale of Pewsey and South Downs flint, and was absent in the Southwestern Chalk flint. The differences in the other elements recorded are perhaps not as striking but statistical analysis can reveal which vary significantly between areas.

The results of the t-tests conducted on the flint samples from the South Downs and North Downs demonstrate that there are three elements that are useful in discriminating between these regions: titanium (p=0.039), cobalt (p=0.042), and zirconium (p=0.007) (figure 6.11).

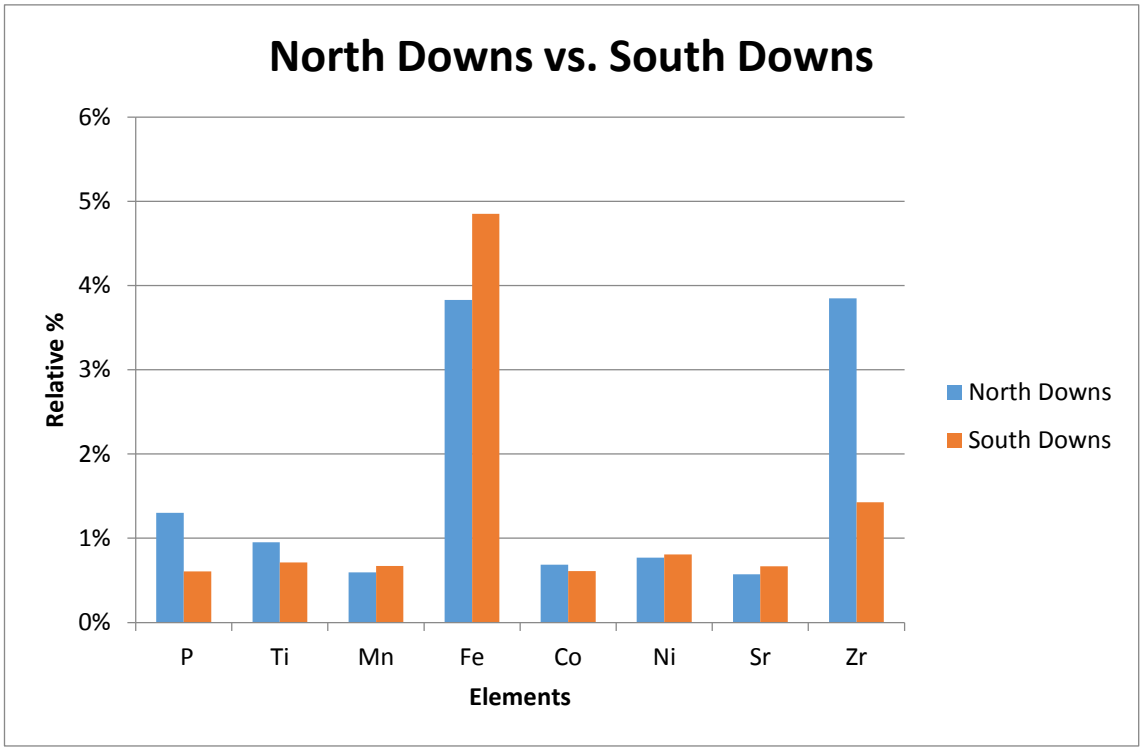


Figure 6.11 – Comparison of flint from North Downs and South Downs

The recorded levels of two elements differed between the South Downs and Southwestern Chalk flint samples; an unpaired t-test demonstrates that cobalt (p=0.001) and nickel (p=0.006) are useful for discriminating these groups (figure 6.12).

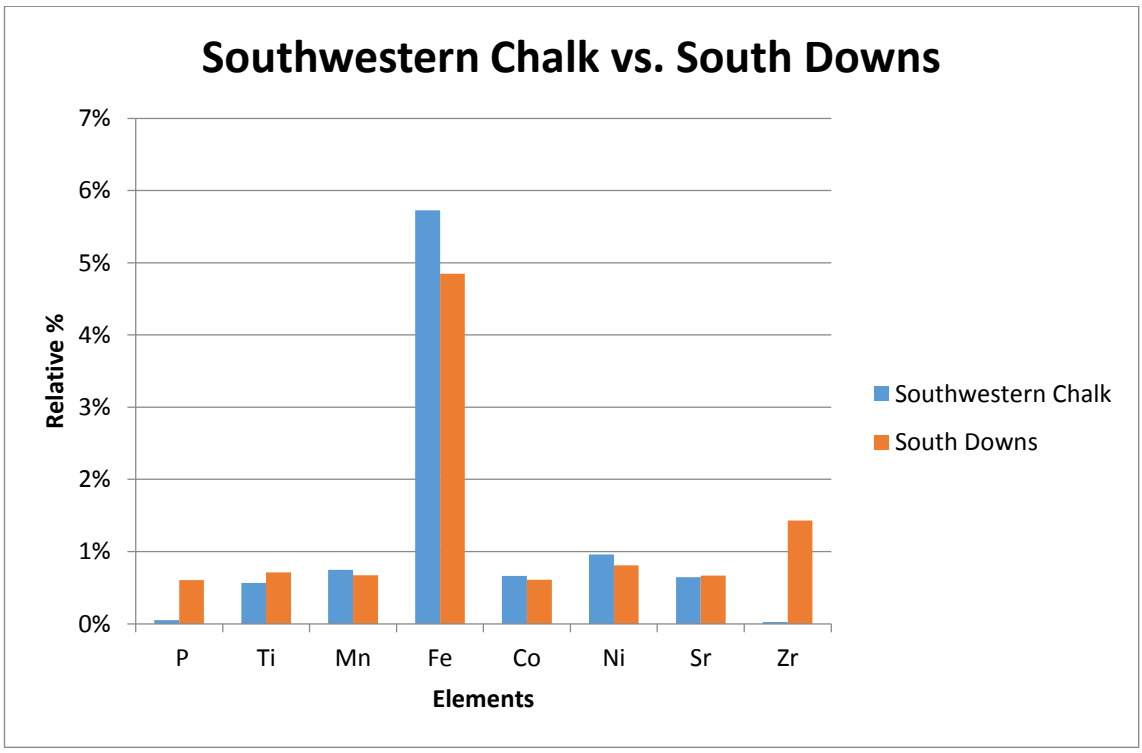


Figure 6.12 – Comparison of flint from North Downs and South Downs

No elements differed between the South Downs flint and Salisbury Plain/Pewsey flint; it was not possible to distinguish between these regions.

The levels of eight elements recorded from the North Downs flint and Southwestern Chalk flint differed, only two differ in a significant manner and provide a means of distinguishing between these groups: titanium (p=0.003) and nickel (p=0.005) (figure 6.13).

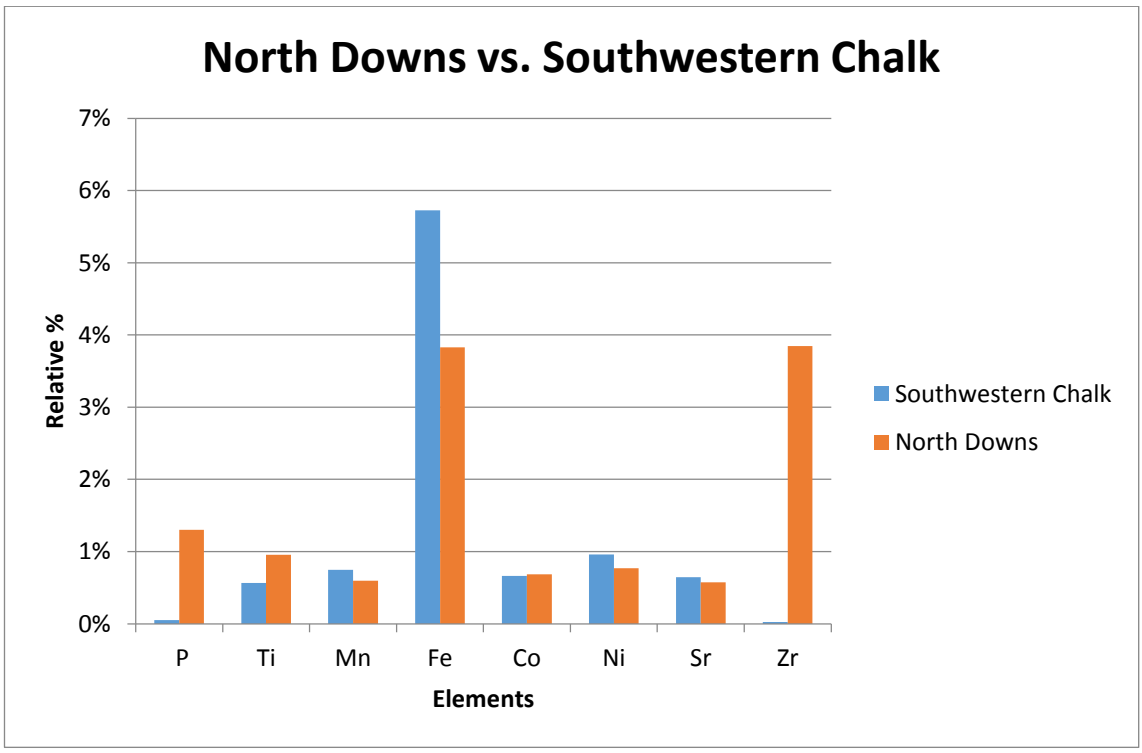


Figure 6.13 – Comparison of flint from North Downs and Southwestern Chalk

The difference recorded in the levels of zirconium (p=0.024) is useful for discrimination between flint from the North Downs and Salisbury Plain/Pewsey area (figure 6.14).

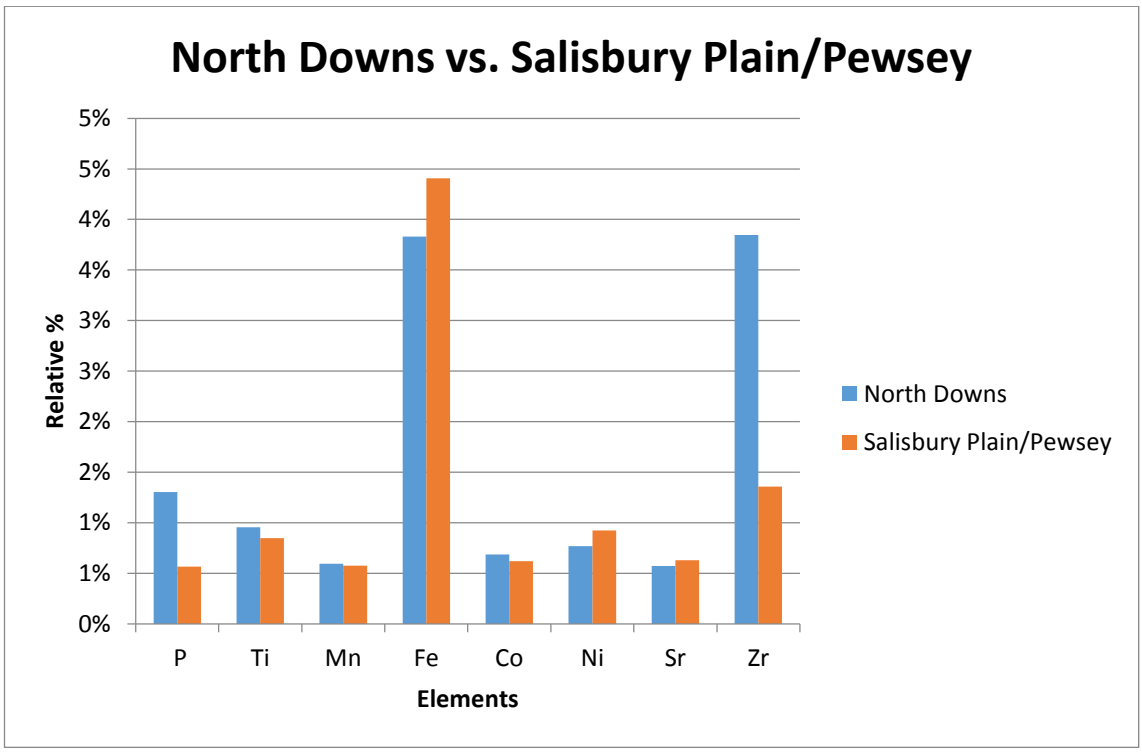


Figure 6.14 – Comparison of flint from North Downs and Salisbury Plain/Pewsey

Distinguishing between the Salisbury Plain/Pewsey samples and those from Southwestern Chalk can be achieved using variation in levels of titanium (p=0.029) and phosphorus (p=0.040) (figure 6.15).

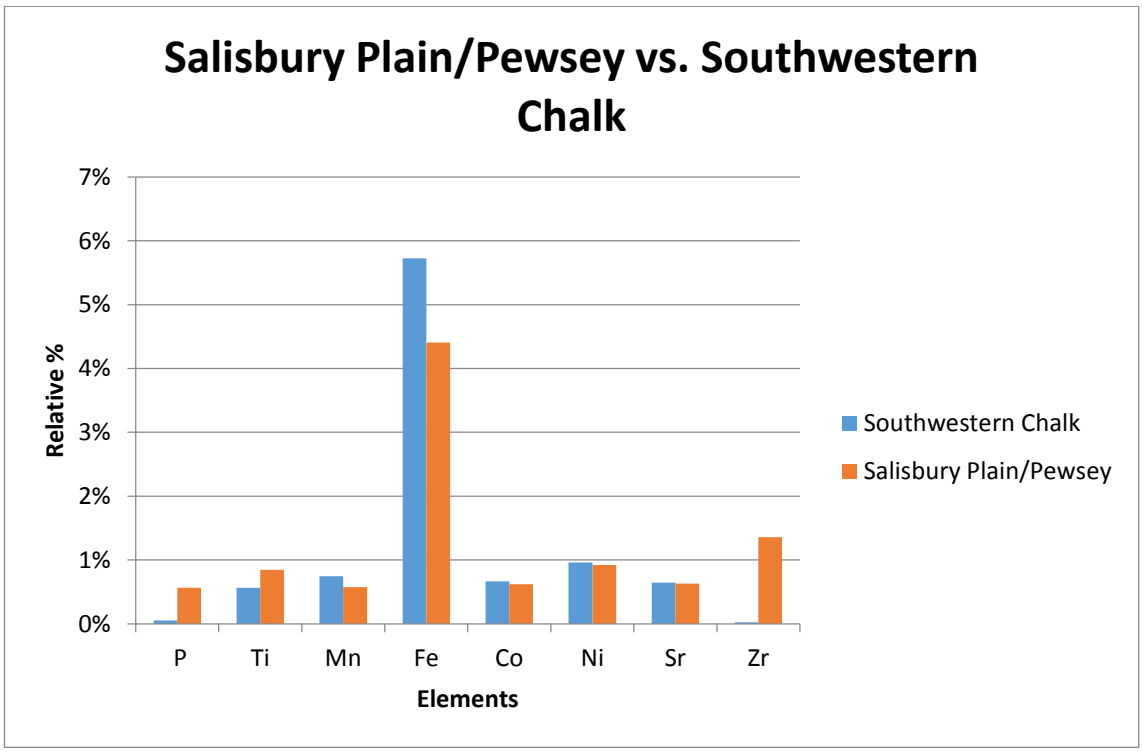


Figure 6.15 – Comparison of flint from Southwestern Chalk and Salisbury Plain/Pewsey

The Southern Chalk Province covers a large swathe of the south of England, and was an important source of flint during various periods in prehistory. The aim of distinguishing between different defined regions within this Province was achieved using an array of elements, although it was not possible to differentiate between South Downs samples and Salisbury Plain/Pewsey samples. The other regions can be distinguished using variation in the levels of one or more of the following five elements: titanium, cobalt, zirconium, nickel, and phosphorus.

6.2.3 *Transitional Chalk province*

The Northern and Southern Chalk provinces in England are considered separately on the basis of their lithostratigraphy and faunal content (Hopson 2005, 1). Between these regions is the

Transitional Province, where the diagnostic features of the Northern and Southern Provinces interdigitate (Mortimore *et. al.* 2001, 7).

Two sites were sampled from the Transitional province: the prehistoric flint mine at Grime's Graves, Norfolk, and Isle of Wight Lane, Dunstable, Bedfordshire. Two nodules from Grime's Graves, and four fragments of nodules from Isle of Wight Lane were analysed. Multiple readings taken from each nodule or nodule fragment were averaged for analysis. The flint from Grime's Graves was very dark grey/black in colour, with infrequent, small white inclusions. The flint from Isle of Wight Lane was pale grey, with large areas of chalky inclusions. Areas containing inclusions were not sampled for pXRF analysis.

Fourteen elements were identified during pXRF analysis: phosphorus, chlorine, potassium, calcium, titanium, manganese, iron, cobalt, nickel, copper, strontium, zirconium, praseodymium, and ytterbium (Figure 6.16).

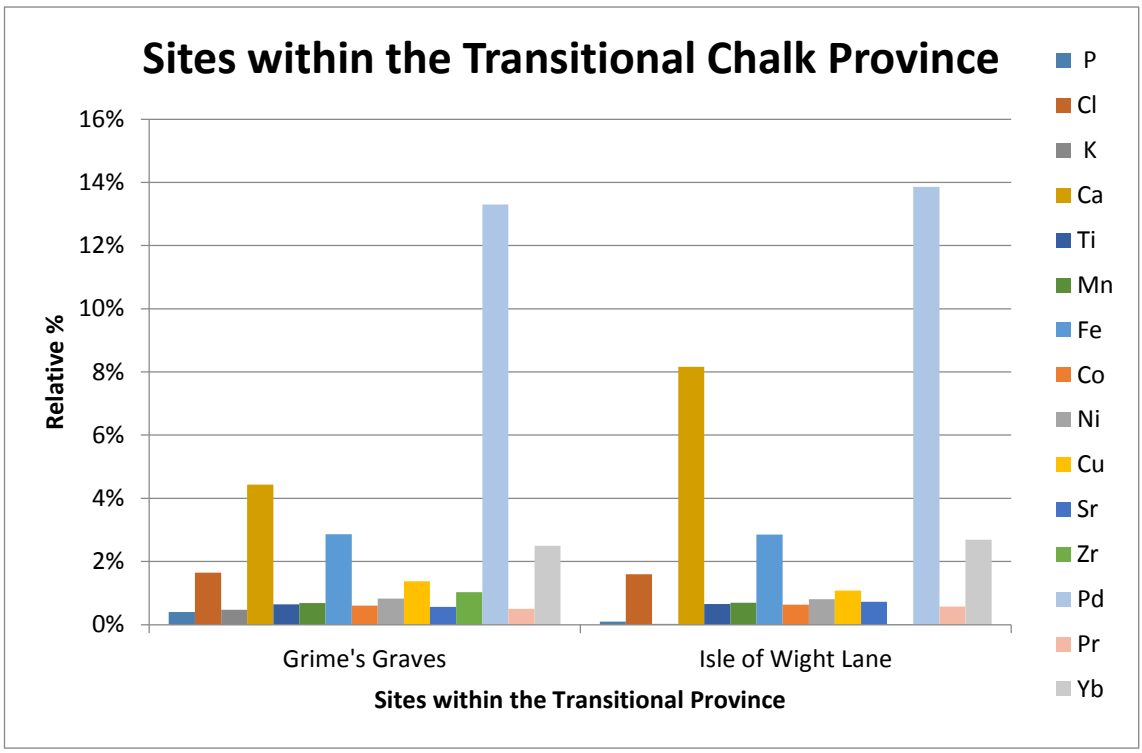


Figure 6.16 - Relative percentages of elements detected in flint from the Transitional Chalk province

The samples from Grime's Graves have lower levels of calcium compared to the flint from Isle of Wight Lane. Only the difference in the level of calcium (p=0.018) between these sites recorded is statistically significant.

6.2.4 *Northern Ireland Chalk province*

The chalk formation in the north of Ireland is largely buried by deposits of Tertiary basalt, resulting in intermittent outcrops of chalk along the northern and eastern coast of Co. Antrim, as well as infrequent, isolated exposures in counties Derry, Tyrone, Armagh, and Down. The thick covering of basalt (up to 2km) has protected the exposures of chalk from erosion (Maliva & Dickson 1997, 105), but has resulted in compression and cementation of the chalk, making it much harder than corresponding chalk in the south of England (Wilson *et. al.* 2001, 346). Analysis of flint samples from the Northern Ireland Chalk province demonstrates that the recorded levels of four elements, calcium, iron, nickel, and silicon vary significantly between patinated and unpatinated surfaces. These elements are not considered in the following discussion.

Seven sites within the Northern Ireland Chalk province were sampled for pXRF analysis: Ballintoy, Portbraddan, Slieve Gallion, White Park Bay, White Rocks, Cloughastucan, and Garron Point. With the exception of Slieve Gallion, these sites are coastal outcrops of flint. Slieve Gallion is an inland location, over 50km from the nearest coastal chalk at White Rocks. The flint collected from the coastal sites was variable in quality, and ranged from light to very dark grey in colour. The flint from Slieve Gallion was orange-brown and largely free of impurities and inclusions. Distinguishing between coastal and inland sources of flint in the

north of Ireland has been demonstrated using electron spin resonance, providing an insight into raw material procurement strategies (Griffiths & Woodman 1987). However, Griffiths and Woodman's study only focused on one coastal site (Carnlough), and sampled flint gathered from the beach; beach flint is a secondary source and may not represent nearby outcrops. Distinguishing between coastal and inland sources of flint was attempted using pXRF analysis. The degree of geochemical variation within the flint from the north of Ireland is not known, and differentiation between different coastal sources was investigated.

The pXRF analysis of the flint samples from the Northern Ireland Chalk province identified ten elements: phosphorus, potassium, titanium, iron, cobalt, nickel, copper, zirconium, praseodymium, and lead. Investigation into patinated flint from the Northern Ireland formation revealed that five elements differ significantly between patinated and unpatinated flint: manganese, strontium, ytterbium, chlorine, and calcium. These elements will not be considered in the following analyses.

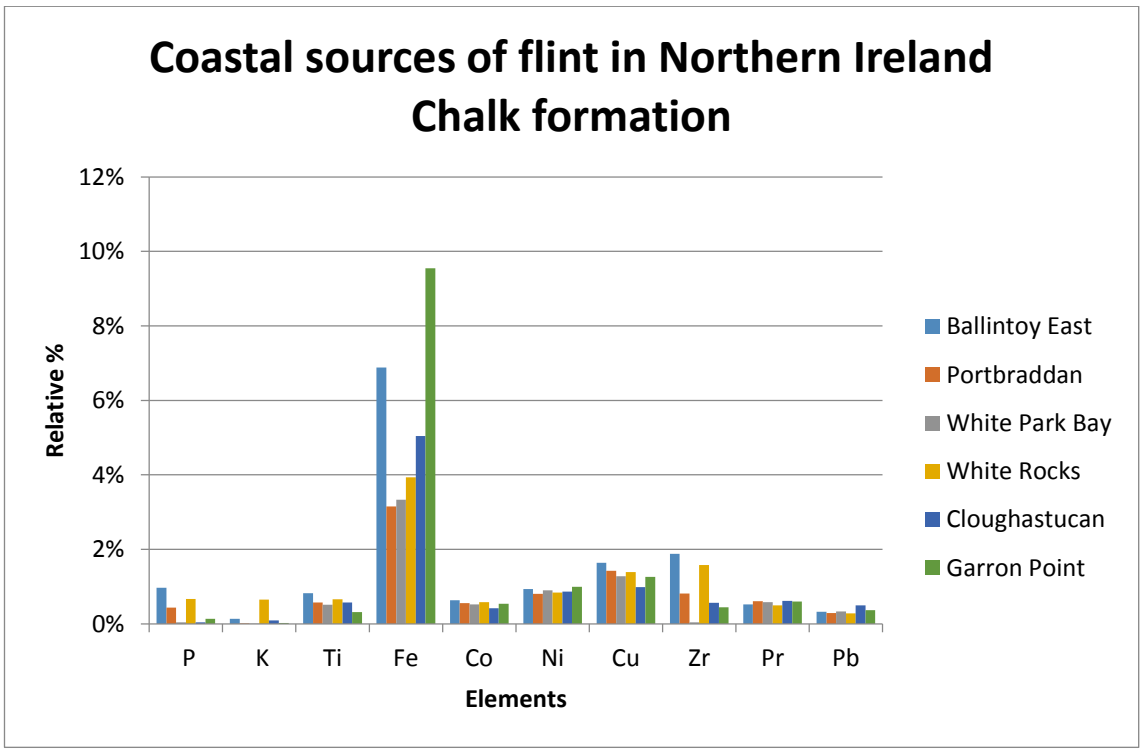


Figure 6.17 – Relative percentages of elements detected in flint from coastal sources in the Northern Ireland Chalk province

Distinguishing between different coastal sources was investigated using pXRF analysis (Figure 6.17). It was possible to differentiate between most of these coastal sources, but through the use of different elements/combinations of elements.

Using the elements outlined above, it was not possible to distinguish between any of the following pairs of sites: Ballintoy East/Portbraddan, Garron Point/White Park Bay, Garron Point/Portbraddan, White Park Bay/Portbraddan, or Cloughastucan/Garron Point.

The majority of sites can be differentiated using variation in levels of one or two elements.

The variation in the levels of potassium (p=0.036) recorded from Ballintoy and White Rocks flint is the only statistically significant difference between these sites (figure 6.18).

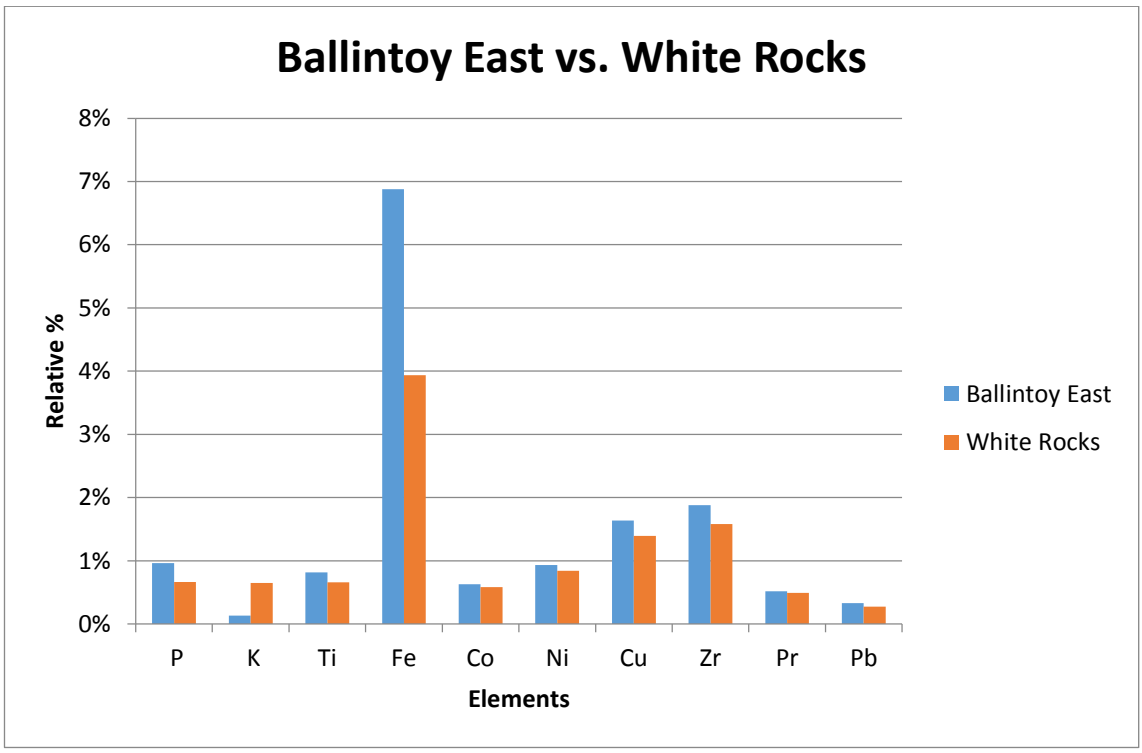


Figure 6.18 – Relative percentages of elements detected in flint from Ballintoy east and White Rocks

Distinguishing between the flint from Ballintoy and flint from White Park Bay was possible on the basis of variation in zirconium levels (p=0.028) (figure 6.19).

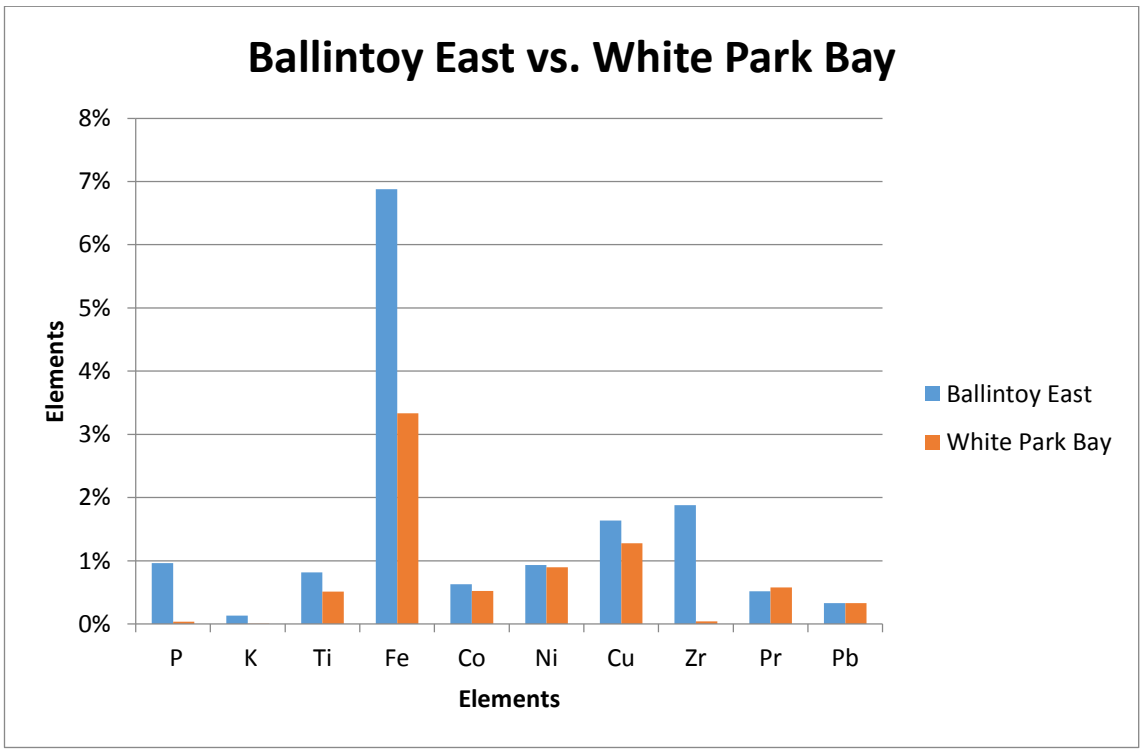


Figure 6.19 – Relative percentages of elements detected in flint from Ballintoy East and White Park Bay

The flint samples from Cloughastucan and White Park Bay could only be distinguished using the differences recorded in the levels of lead (p=0.049) (figure 6.20).

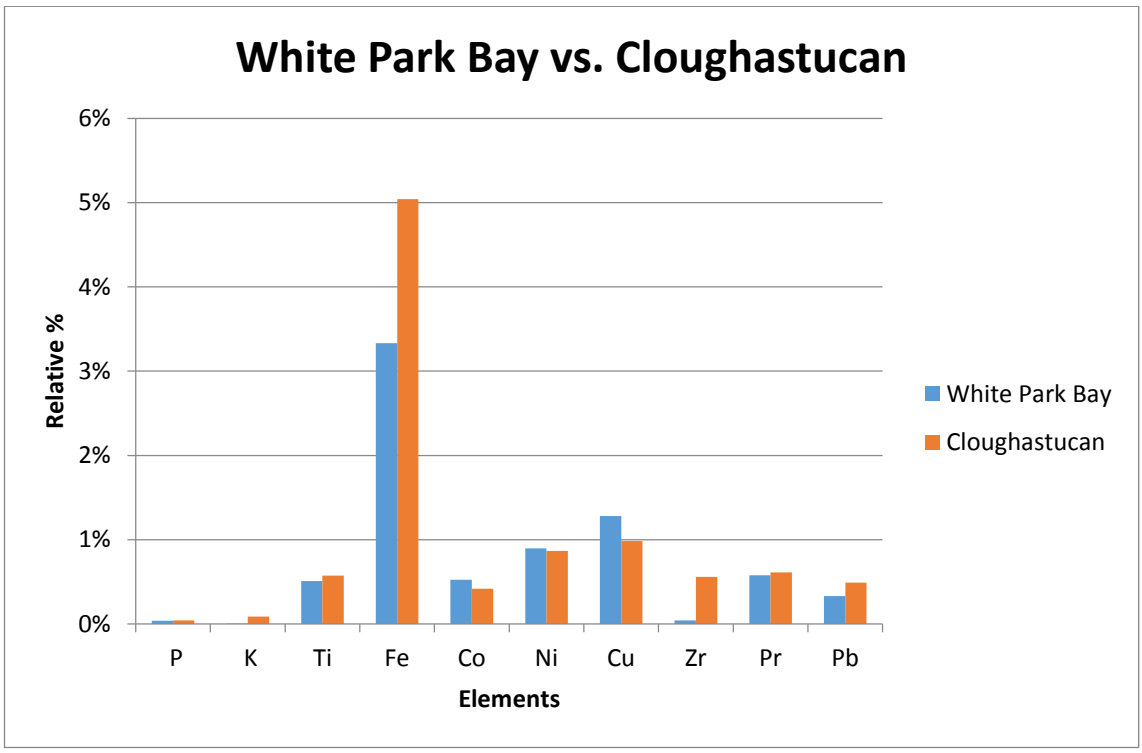


Figure 6.20 – Relative percentages of elements detected in flint from Cloughastucan and White Park Bay

Despite the visible difference between the recorded levels of iron between Ballintoy and Garron Point (Figure 6.21), only the variation in phosphorus (p=0.035) and zirconium (p=0.011) proved to be statistically significant.

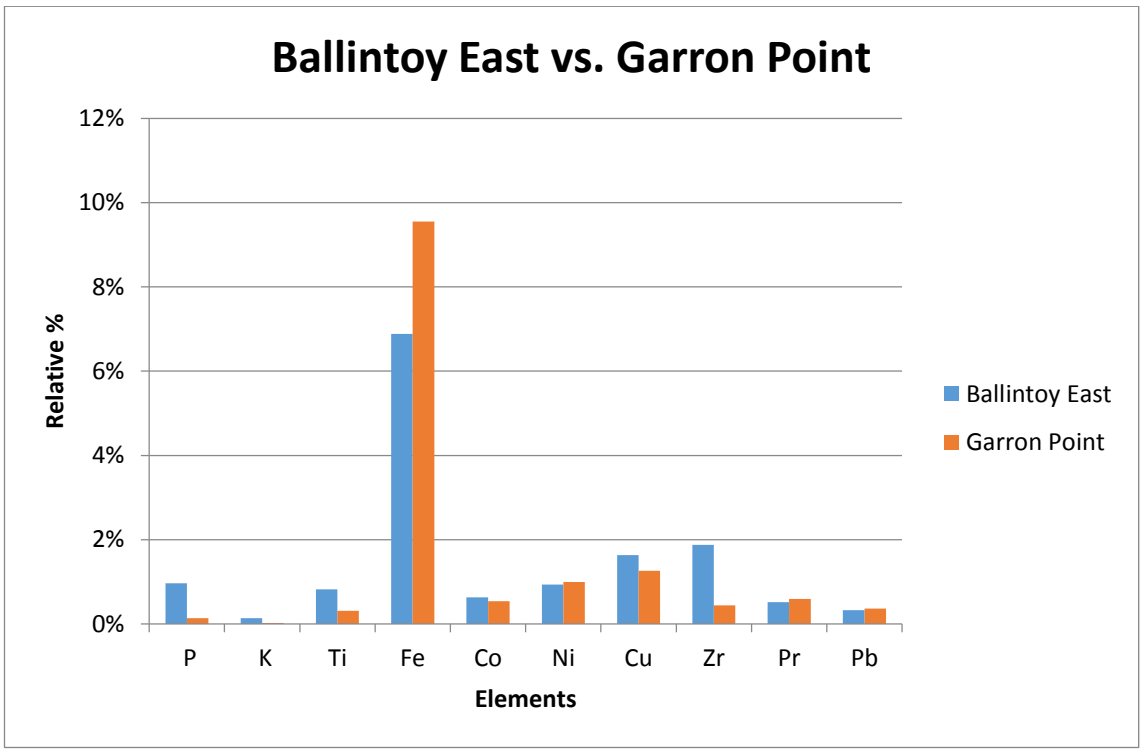


Figure 6.21 – Relative percentages of elements detected in flint from Ballintoy East and Garron Point

The flint from Ballintoy and Cloughastucan can be differentiated using the recorded levels of phosphorus (p=0.025) and zirconium (p=0.012) (figure 6.22).

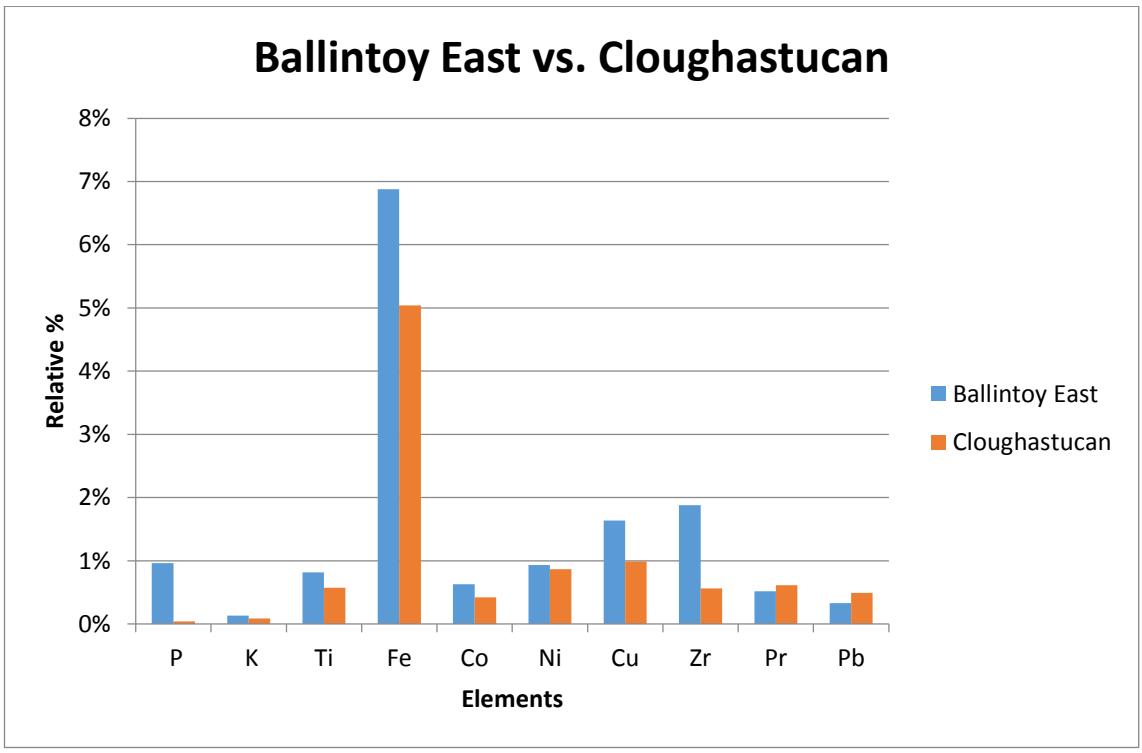


Figure 6.22 – Relative percentages of elements detected in flint from Ballintoy East and Cloughastucan

Flint samples from Cloughastucan and Portbraddan can be differentiated through differing levels of two elements; lead (p=0.022) and copper (p=0.038) (figure 6.23).

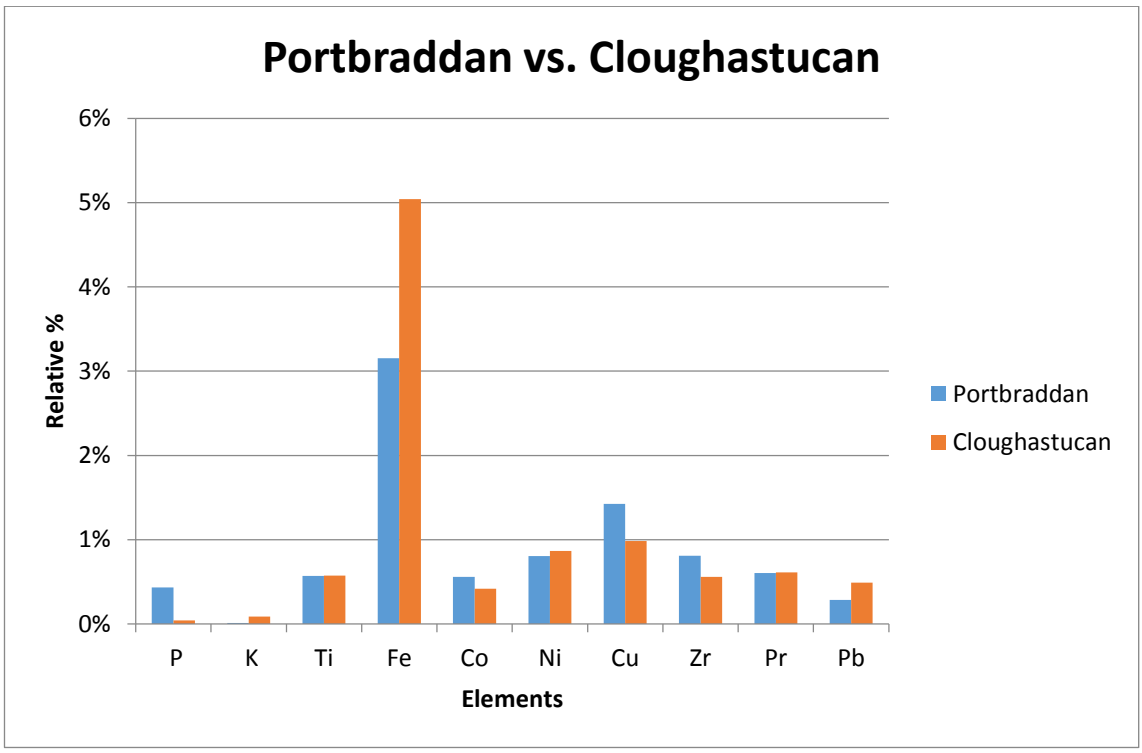


Figure 6.23 – Relative percentages of elements detected in flint from Portbraddan and Cloughastucan

The samples from White Rocks and Portbraddan can be distinguished using statistically significant differences recorded in the levels of potassium (p=0.013) and iron (p=0.03) (figure 6.24).

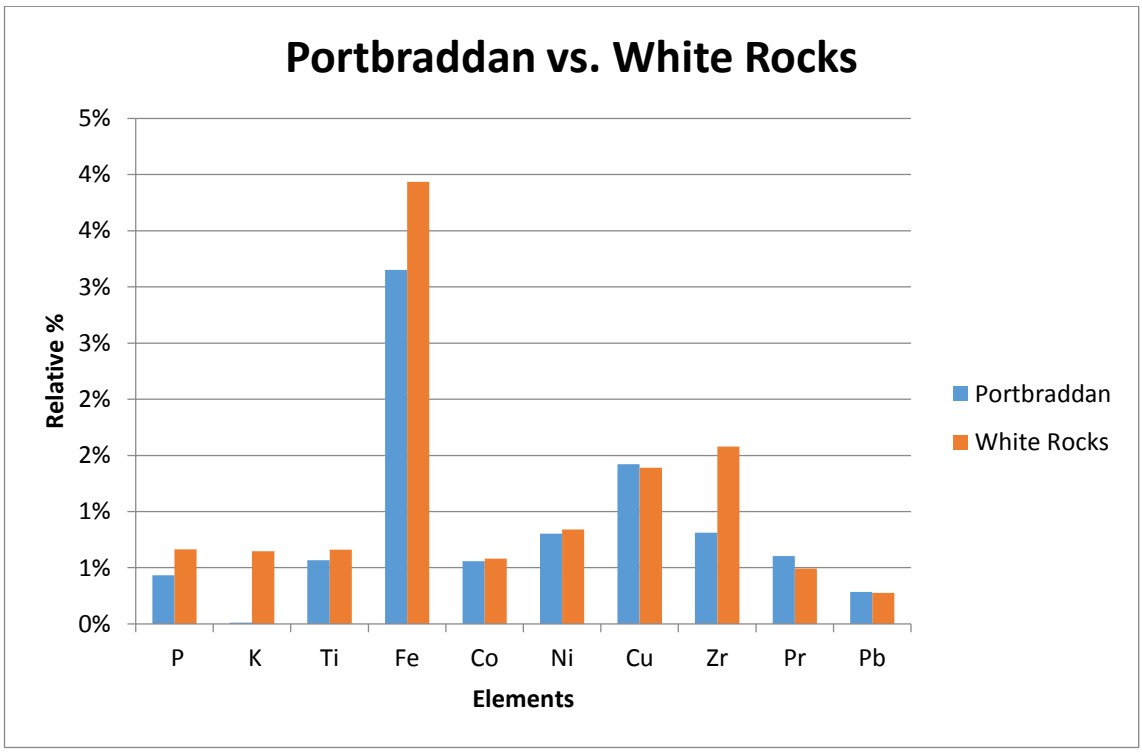


Figure 6.24 – Relative percentages of elements detected in flint from Portbraddan and White Rocks

Three sites could be distinguished on the basis of variation in three or more elements. The recorded levels of three elements, phosphorus (p=0.003), potassium (p=0.014), and zirconium (p=0.01), differed between the flint from Garron Point and White Rocks (figure 6.25).

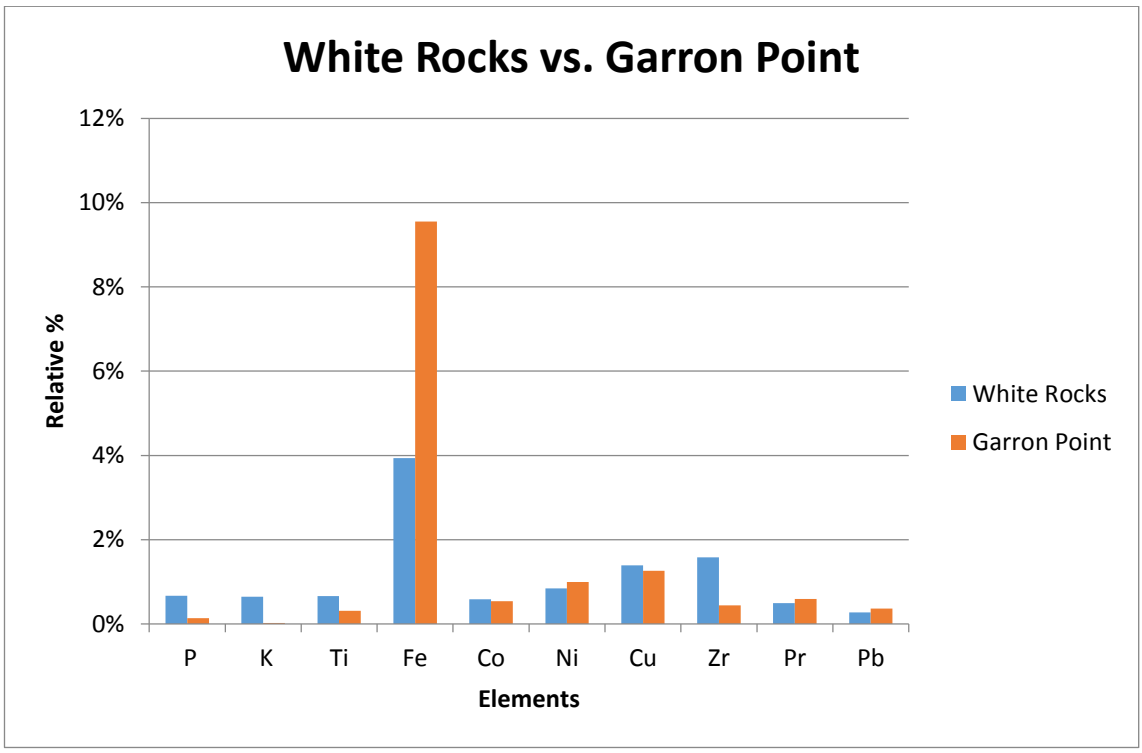


Figure 6.25 – Relative percentages of elements detected in flint from Garron Point and White Rocks

The differences in the levels phosphorus (p=0.001), potassium (p=0.012), titanium (p=0.011), and zirconium (p=0.002) between White Park Bay and White Rocks are statistically significant, facilitating differentiation between these two sites (figure 6.26).

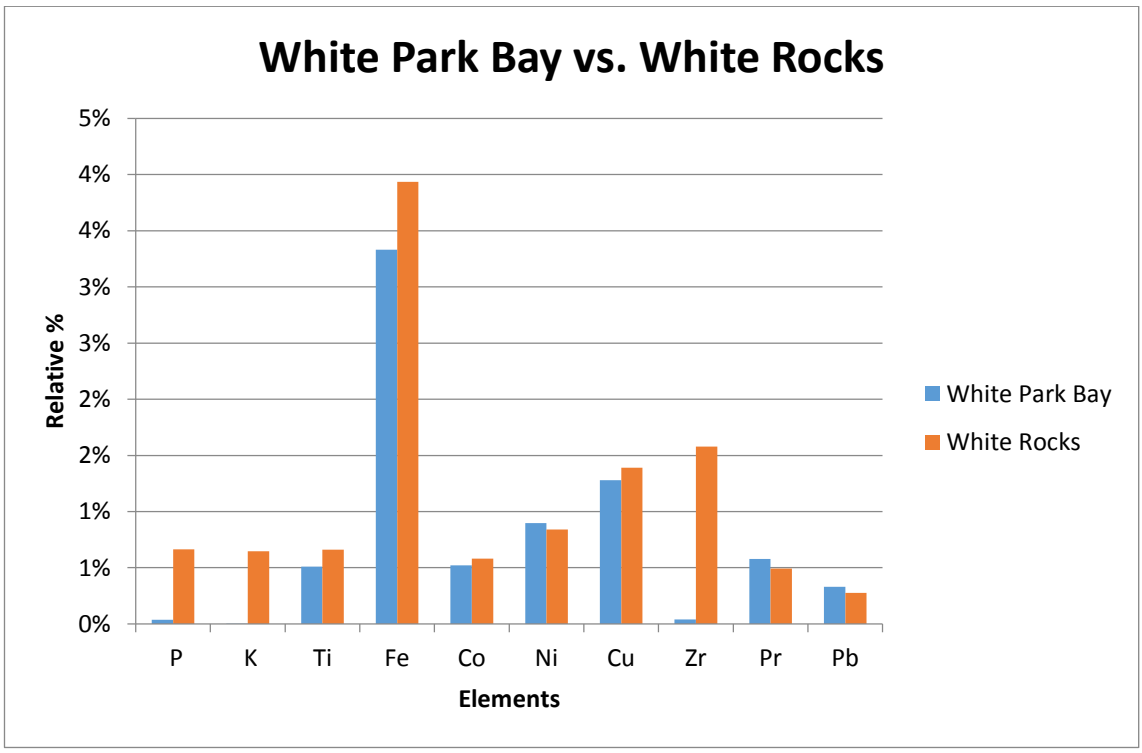


Figure 6.26 – Relative percentages of elements detected in flint from White Park Bay and White Rocks

Flint samples from White Rocks and Cloughastucan can be differentiated using variation in the levels of phosphorus (p=0.001), potassium (p=0.021), lead (p=0.008), copper (p=0.0001), zirconium (p=0.014), and praseodymium (p=0.005) (figure 6.27).

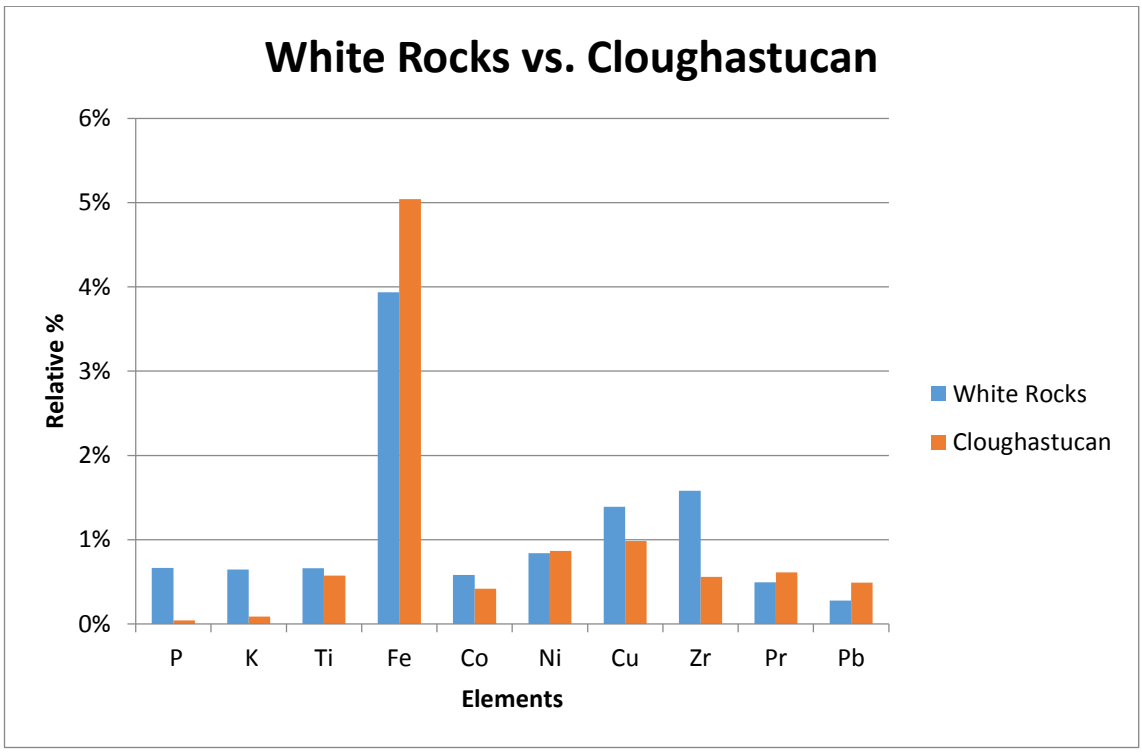


Figure 6.27 – Relative percentages of elements detected in flint from Cloughastucan and White Rocks

The sources of flint in the north of Ireland outcrop along stretches of the coastline in chalk cliffs, although the chalk formation extends underneath the overlying basalt plateau and outcrops intermittently further inland. It is possible to distinguish between flint samples from most areas on the coast using pXRF analysis, using a variety of elements. Differentiation between certain sites was more difficult than for others.

The distance between coastal sample collection sites did not appear to improve the likelihood of distinguishing between the flint. For example, White Park Bay and White Rocks are little over 15km apart but the flint samples demonstrate statistically significant differences in the recorded levels of phosphorus, potassium, zirconium, and titanium. In contrast, White Park

Bay and Garron Point are c.44km apart, but cannot be distinguished using any of the recorded elements.

Distinguishing between flint from an inland source and flint from coastal outcrops of chalk was attempted using pXRF analysis. Inland and coastal flint from Ireland can be distinguished using variation in levels of three elements: phosphorus (p=0.001), titanium (p=0.005), and zirconium (p=0.0002). The variation in zirconium is particularly statistically significant. Figure 6.28 illustrates the differences in relative percentages of elements detected in flint samples from both coastal and inland locations within the Northern Ireland Chalk formation.

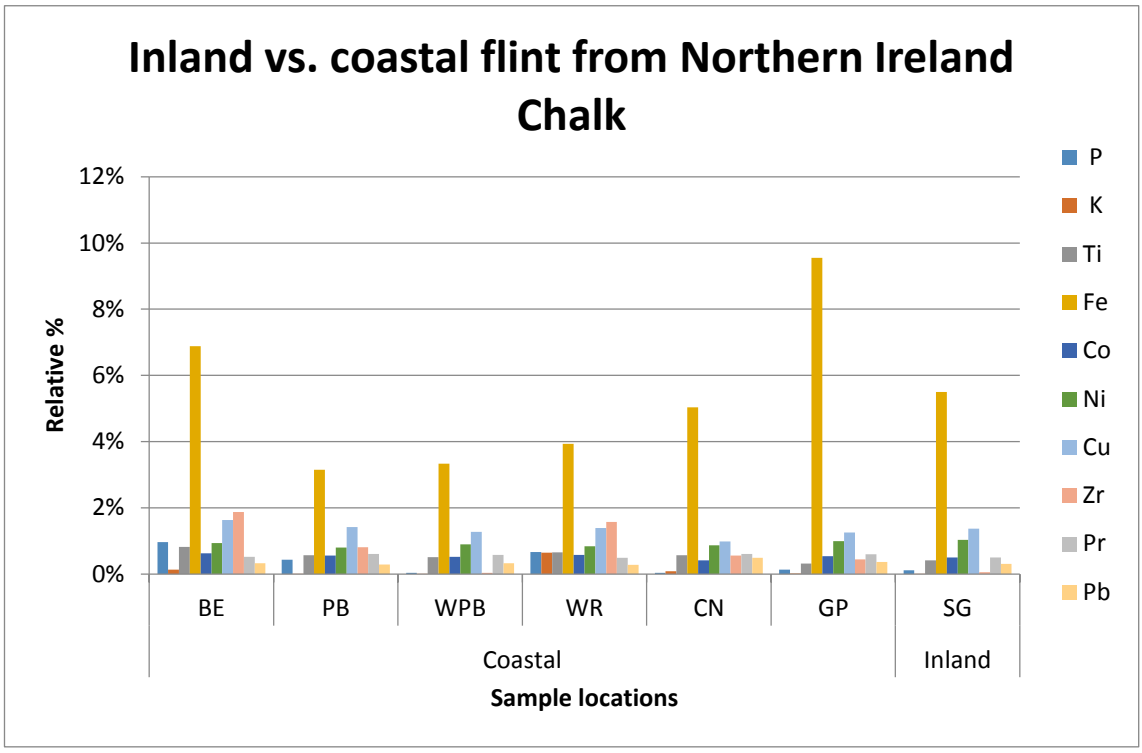


Figure 6.28 – comparison of flint collected from inland vs. coastal locations within the Northern Ireland Chalk formation

6.2.5 *Differentiating Chalk provinces within Britain*

Provenancing within Britain was attempted using pXRF analysis. This section presents results that demonstrate whether the different flint-producing areas of chalk within England (Northern, Southern, and Transitional chalk provinces) can be separated using geochemical analysis. As with the analyses above, any elements that showed statistically significant differences between patinated and unpatinated surfaces will not be considered.

The flint samples from the Northern Chalk province and the Transitional Chalk province demonstrated differences in the levels of sixteen elements: chlorine, potassium, calcium, titanium, manganese, iron, cobalt, nickel, copper, zinc, strontium, cerium, praseodymium, and ytterbium. Of these, the levels of eight elements differed in statistically significant ways (figure 6.29).

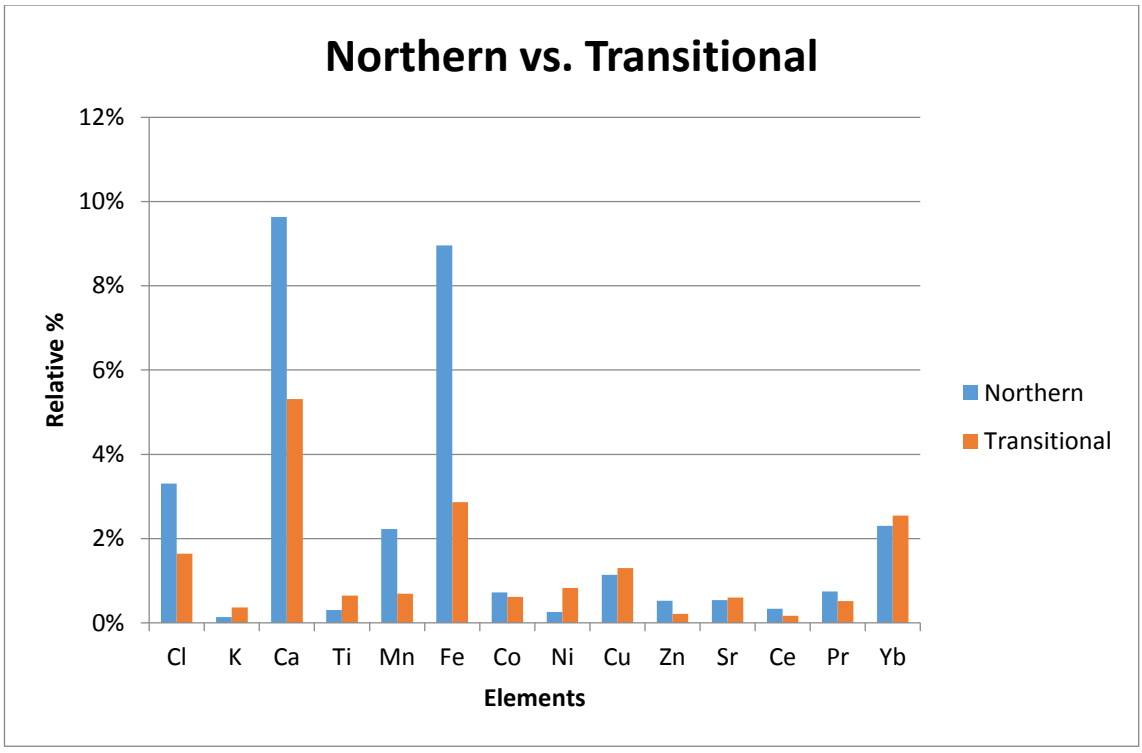


Figure 6.29 – Relative percentages of elements detected in flint samples collected from the Northern and Transitional Chalk provinces

The results of the t-tests illustrate that flint from the Northern and Transitional Chalk provinces can be differentiated using variation in the levels of calcium (p=0.039), titanium (p=0.0007), manganese (p=0.003), cobalt (p=0.025), thorium (p=0.004), cerium (p=0.003), praseodymium (p=0.001), and ytterbium (p=0.006).

The Northern and Southern Chalk province flint samples have differing levels of nine elements: phosphorus, titanium, manganese, iron, cobalt, nickel, zinc, strontium, and cerium (figure 6.30).

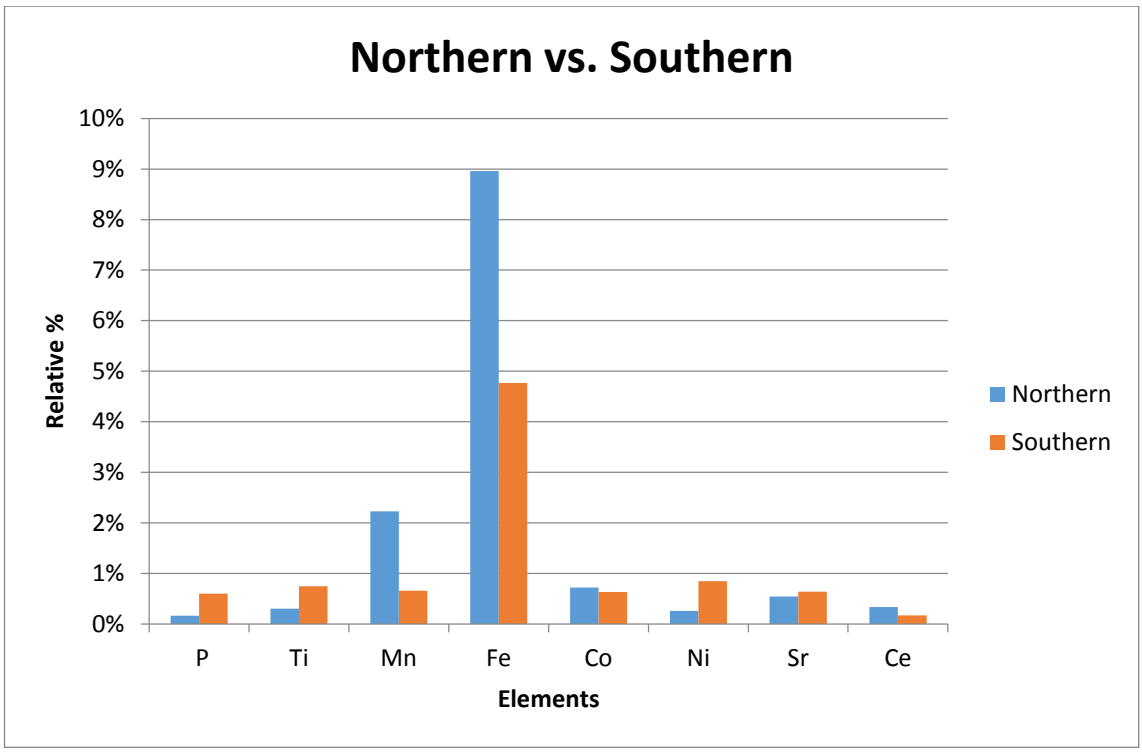


Figure 6.30 – Relative percentages of elements detected in flint samples collected from the Northern and Southern Chalk provinces

The results of the t-tests demonstrate that the Northern and Southern Chalk provinces can be distinguished using variation in the relative percentages of fewer elements than the Northern and Transitional Chalk provinces. The differences in four elements provide statistically

significant *p* values: manganese (*p*=0.002), iron (*p*=0.0005), cobalt (*p*=0.002), and cerium (*p*=0.002).

The recorded levels of nine elements varied between the flint samples from the Southern and Transitional Chalk provinces: phosphorus, titanium, manganese, cobalt, iron, nickel, zinc, strontium, and cerium. None of these varied significantly (figure 6.31).

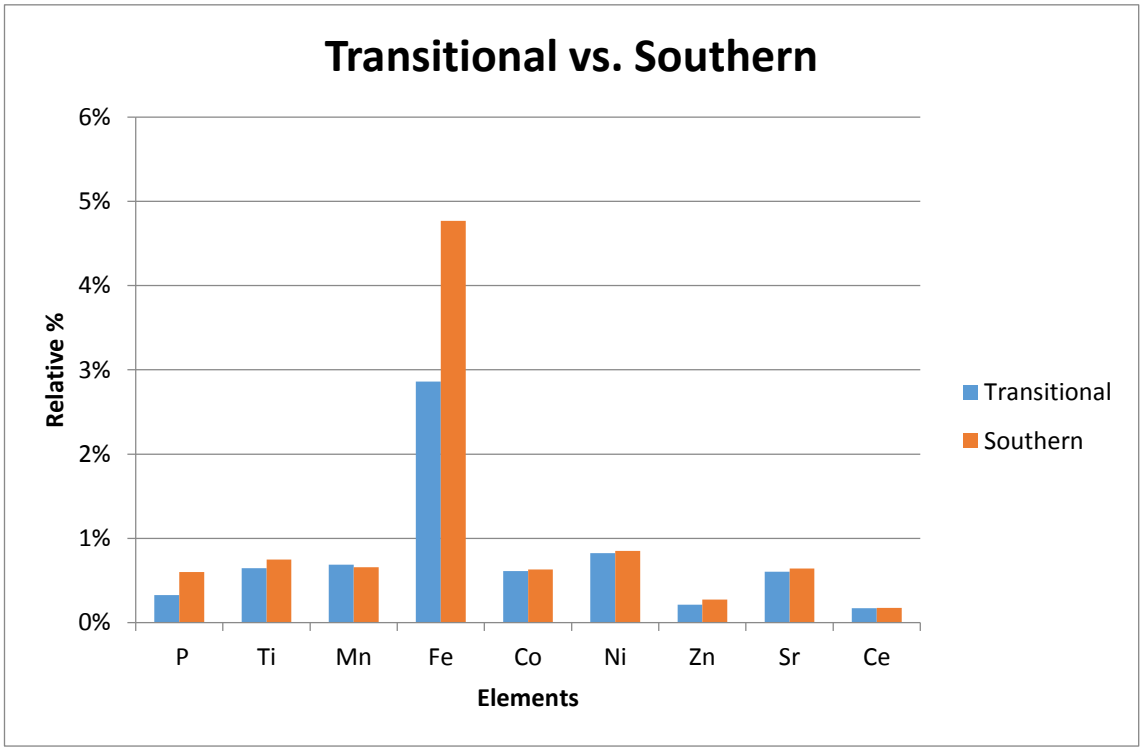


Figure 6.31 – Relative percentages of elements detected in flint samples collected from the Transitional and Southern Chalk provinces

6.2.6 *Differentiating between Chalk provinces in Britain and Ireland*

Analysis of flint from chalk provinces in Britain and Ireland revealed differences in the levels of nine elements: phosphorus, chlorine, potassium, titanium, manganese, cobalt, copper, praseodymium, and ytterbium (figure 6.32). The differences in three of these elements from the Northern Ireland Chalk province and English Chalk flint provided statistically significant *p*

values: iron (p=0.003), zinc (p=0.0007), and cerium (p=0.008). These results indicate that flint from English Chalk outcrops can be distinguished from flint from the Northern Ireland Chalk provinces on the basis of variations in the levels of these elements.

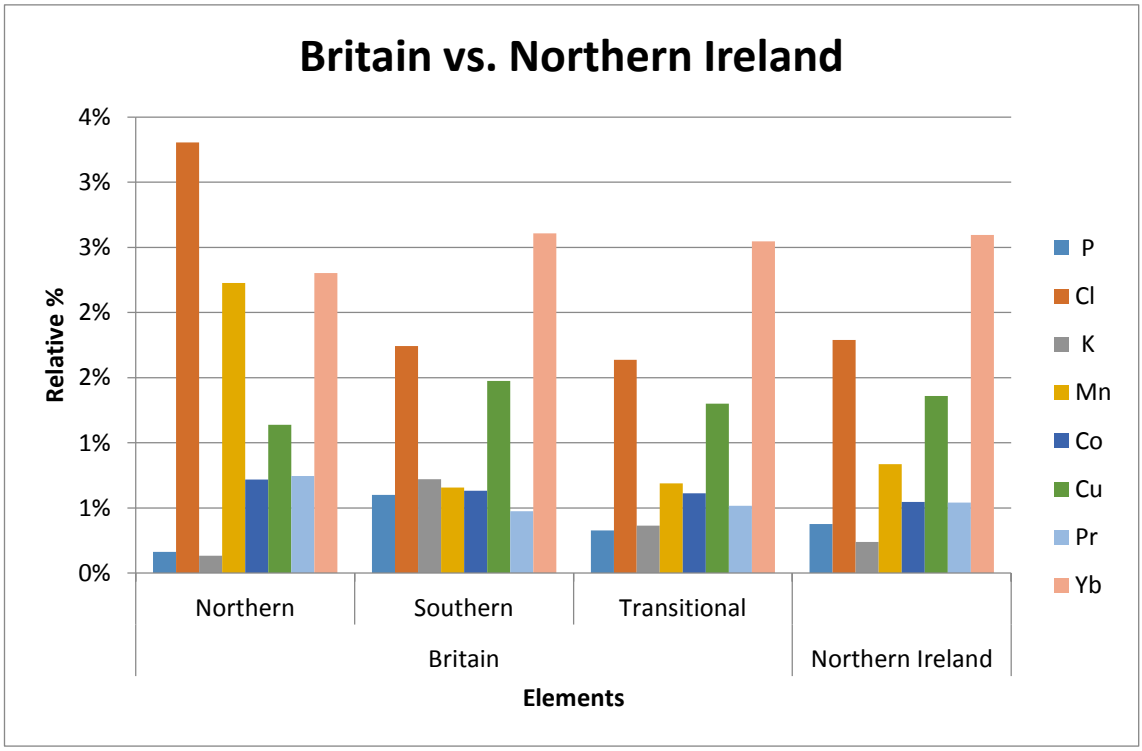


Figure 6.32 – Relative percentages of elements detected in flint samples collected from Britain and Northern Ireland

6.3 Portable X-ray fluorescence results conclusion

This chapter has outlined the results of portable X-ray fluorescence analysis of flint samples from the Northern Ireland, Northern, Southern, and Transitional Chalk provinces. The aim was to determine if non-destructive pXRF analysis can distinguish between flint sourced from different geographic regions in Britain and Ireland, and whether the patina commonly found on flint adversely affects geochemical provenancing.

As demonstrated above, patinated areas on flint can adversely impact on geochemical provenancing. The samples of flint from the Southern Chalk province displayed significant differences in the levels of silicon, copper, ytterbium, chlorine, and praseodymium between patinated and unpatinated surfaces. However, the samples from the Salisbury Plain/Vale of Pewsey did not display any differences between patinated flint and unpatinated flint, whereas the samples from the North Downs did have significant variation in the levels of silicon, chlorine, potassium, calcium, and copper between patinated and unpatinated surfaces. Samples from the Northern Ireland Chalk province displayed significant variation in the levels of manganese, strontium, ytterbium, chlorine, and calcium.

Differentiating between chalk provinces in Britain could be achieved. The Northern Chalk province could be distinguished from the Transitional province using statistically significant variations of seven elements (calcium, titanium, manganese, cobalt, cerium, praseodymium, and ytterbium); the Northern and Southern Chalk provinces can also be distinguished using a multitude of elements (manganese, iron, cobalt, copper, cerium). The Southern and Transitional provinces could not be distinguished. Within each of the Chalk provinces are more discrete geographic regions, e.g. South Downs, Yorkshire Wolds, which were also investigated to determine if they can be differentiated on the basis of their geochemistry.

It was possible to differentiate between all of the areas within the Southern Chalk province, with one exception; it was not possible to distinguish between flint from the South Downs and flint from Salisbury Plain/Pewsey.

One of the main research questions was whether pXRF analysis can distinguish between flint from Britain and flint from Ireland. It was anticipated that the flint samples from Britain and

Ireland could be distinguished using a greater number of elements, however it was achieved using only three elements: iron, zinc, and cerium.

Samples collected from the Northern Ireland Chalk province were predominantly collected from coastal sites, as this is where the chalk outcrops are most accessible. One sampling site was located inland, at Slieve Gallion. Differentiating between coastal and inland sources could be achieved using variation in the recorded levels of titanium, phosphorus, and zirconium. The six sampling locations on the coast (White Park Bay, White Rocks, Ballintoy, Portbraddan, Cloughastucan, and Garron Point) were also investigated to assess the level of geochemical variation within the Northern Ireland Chalk province. It was not possible to distinguish between all sampling locations; however the majority can be distinguished using one or more elements.

This chapter has outlined the results of the pXRF analysis of flint samples collected from Britain and Ireland and found that it is possible to distinguish between the islands, and additionally that it is possible to distinguish between more discrete geographic regions within both Britain and Ireland (with few exceptions). It has also demonstrated the effect of patina on attempts at geochemical provenancing, and provided indications that patina is not necessarily a stumbling block to provenancing artefacts but that the impact of patina is not predictable across different Chalk provinces and should be taken into account.

7.0 INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY RESULTS

This chapter will outline the results of the inductively coupled plasma-mass spectrometry (ICP-MS) analysis. This was undertaken using the methodology as described in Chapter 5. The results of the ICP-MS analysis are available in Appendix 7.1. This chapter will detail the results of the ICP-MS analysis in relation to the research questions previously established, and published geochemical analyses of flint.

The ICP-MS results were generated in Microsoft Excel, providing elemental concentrations in parts per billion (ppb). Differences between the results from the flint provinces established were analysed for statistical significance. As with the previous chapter, only the statistically significant results are outlined here, full results of all the t-tests performed are included in appendix 7.2. This chapter considers the effect of patinated surfaces on attempts at geochemical provenancing, before investigating differences between each of the source areas of flint within Britain and Ireland.

7.1 Effects of patina on geochemical provenancing

The formation and potential effects of patinated flint for geochemical provenancing has been described in the previous chapter (6.1). It was not known if patina would have a detrimental effect, providing elevated or depleted levels of certain elements, therefore patinated surfaces were removed prior to analysis. Some samples of patina were deliberately retained and tested to provide a comparison with unpatinated flint.

Four samples of patinated flint from the Northern Ireland Chalk formation and six samples from the Southern Chalk province were analysed. It proved difficult to find areas of patina that were sufficiently thick and free of other potential contaminants such as inclusions or staining. Thirteen elements were identified and quantified using ICP-MS: sodium, magnesium, aluminium, chromium, manganese, iron, cobalt, copper, rubidium, strontium, cadmium, barium, and lead. The results for sodium and iron are presented on separate graphs as the high readings from these elements obscured patterns in the rest of the data.

7.1.1 Northern Ireland Chalk formation

Samples from three sites from the Northern Ireland Chalk formation were suitable to investigate the effect of patina: Slieve Gallion, White Rocks, and Garron Point. The patinated surfaces of the flint from Slieve Gallion were dark brown/orange, whereas the patina from White Rocks and Garron Point were dark grey. This may be due to the context in which the flint was found; the Slieve Gallion samples were found as large nodules in soil, whereas the White Rocks and Garron Point samples were recovered from beaches. Slieve Gallion flint was exposed to a range of minerals from the soil, the White Rocks and Garron Point flint was exposed to air and seawater.

Of the levels recorded of the thirteen elements identified, none of these differences were statistically significant (figure 7.1 and 7.2).

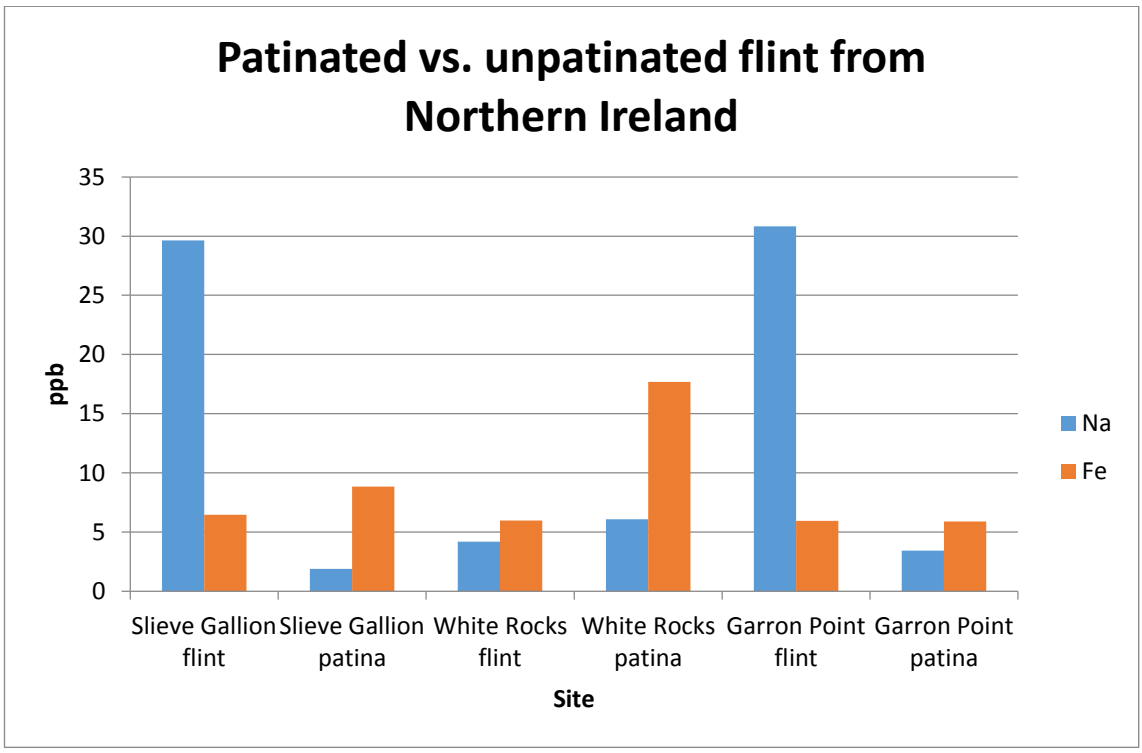


Figure 7.1 – results for patinated and unpatinated flint from Northern Ireland

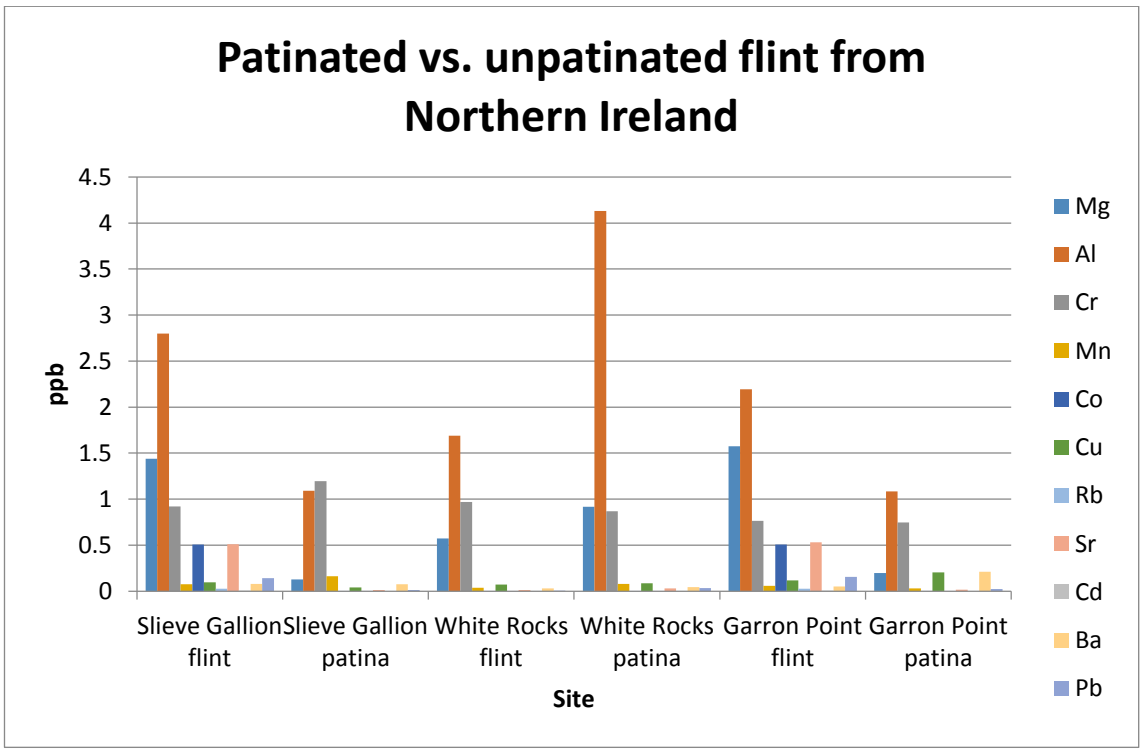


Figure 7.2 – results for patinated and unpatinated flint from Northern Ireland

7.1.2 Southern Chalk province

Three sites in the Southern Chalk province provided samples that were suitable for analysis: Cissbury, Harrow Hill, and Southwick Hill. The patinated surfaces of the Cissbury flint were light grey/white, whereas the Harrow Hill and Southwick Hill flint patinas were dark grey. The unpatinated flint ranged from very light grey to dark grey/black at all three sites. The lighter colour of the Cissbury patinated flint may be a reflection of the depositional context; light, chalky soil. As above, the results for sodium and iron (figure 7.3) are depicted separately with the addition of calcium and potassium, as are the results for magnesium, aluminium, and chromium (figure 7.4), the remainder of the data is presented in figure 7.5.

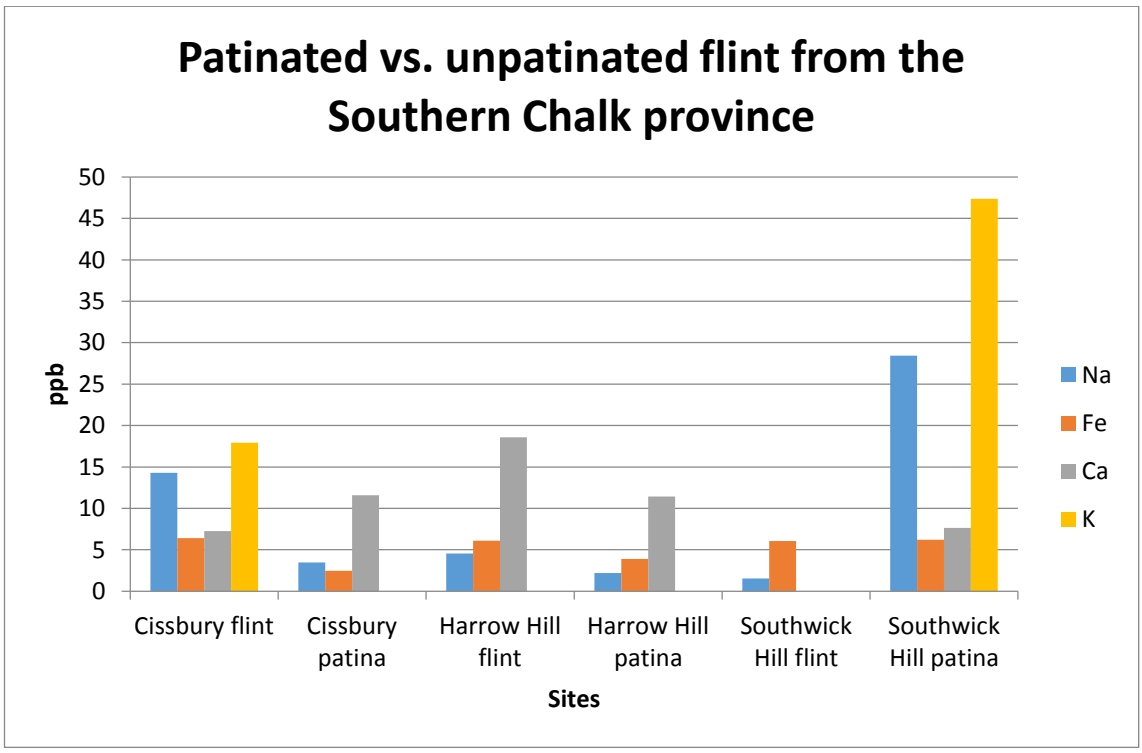


Figure 7.3 – results for patinated and unpatinated flint from Southern Chalk province

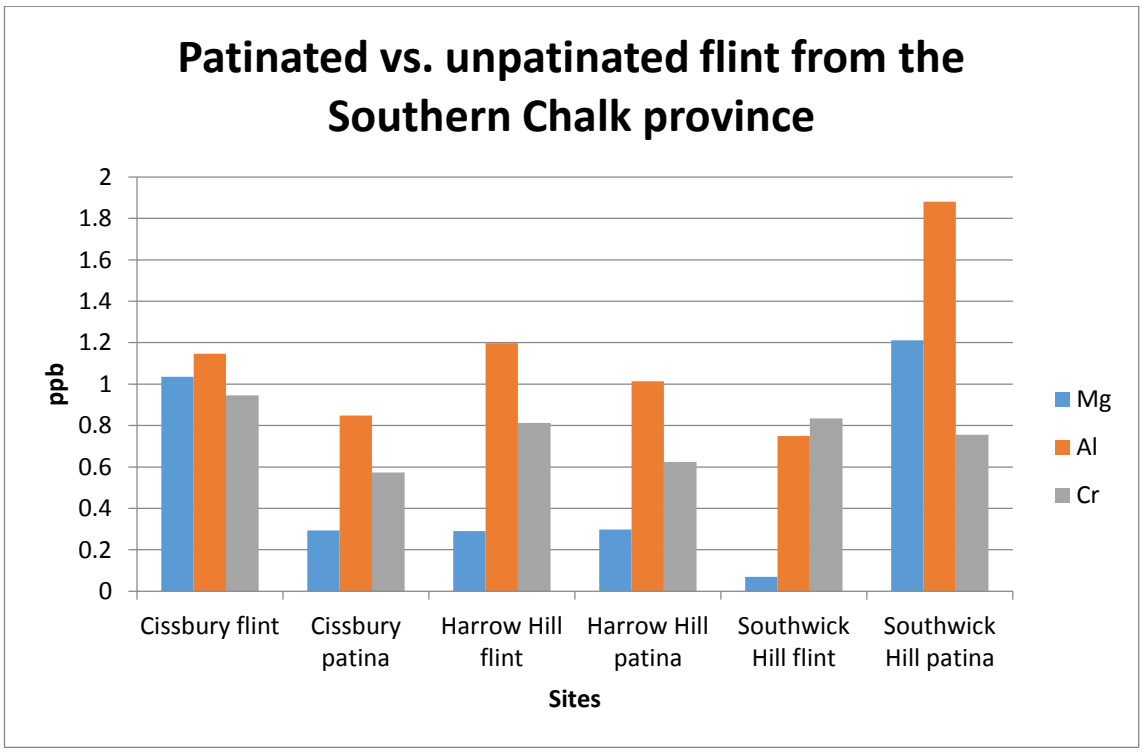


Figure 7.4 – results for patinated and unpatinated flint from Southern Chalk province

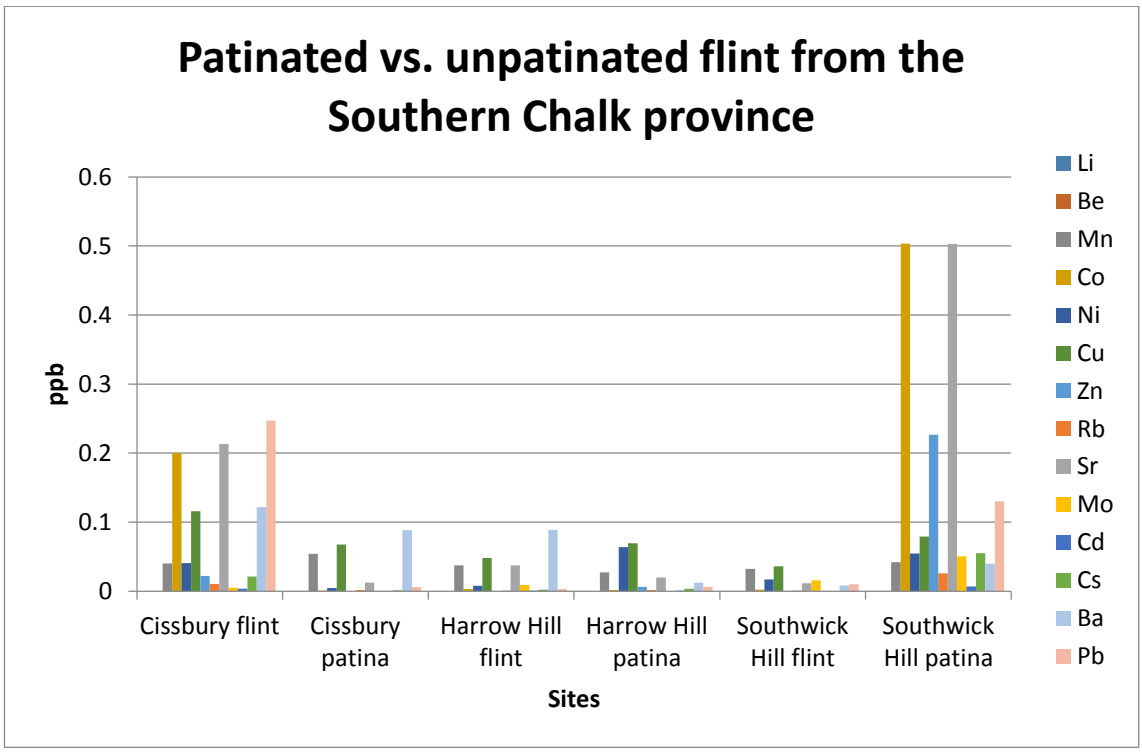


Figure 7.5 – results for patinated and unpatinated flint from Southern Chalk province

Despite the often marked difference in appearance between patinated and unpatinated flint from the Southern province, the only statistically significant difference was found in the levels of chromium recorded (p=0.046).

The pXRF results from the analysis of patinated and unpatinated flint demonstrated that were significant and unpredictable interferences from elevated or depleted levels of elements in patinated surfaces. Patinated and unpatinated samples from the Southern Chalk province analysed using pXRF showed variation in the levels of nine elements; the ICP-MS results do not corroborate this, with the exception of variation in concentrations of chromium in flint from the Southern Chalk province. Analysis of samples from the Northern Ireland Chalk province using pXRF demonstrated that the levels of five elements differ significantly between

patinated and unpatinated flint. The ICP-MS results show no statistically significant variation in samples from this area.

The results illustrated above are not representative of the entirety of flint-bearing chalk formations in Britain and Ireland, but provide an indication that patinated surfaces may not be a barrier to provenancing.

7.2 Flint-producing areas within Britain and Ireland

The areas of flint-bearing chalk geology have been described in 6.2; this chapter uses the same terminology to refer to geographic areas of Britain and Ireland (see figure 6.1).

7.2.1 Northern Chalk province

Eight sites within the Northern Chalk province provided suitable samples for ICP-MS analysis: Rifle Butts, Middleton Quarry, Sledmere/Malton, Arras Hill, Welton-le-Wold, Mill Hill, North Ormsby, and Malton. As stated in 6.2.1, the quality of this flint was variable and it was difficult to isolate fragments of flint suitable for ICP-MS analysis without patina, inclusions, or cortex.

Using pXRF it was possible to distinguish between flint from the Yorkshire and Lincolnshire Wolds using relative percentages of potassium, titanium, manganese, cerium, ytterbium, and chlorine. Chlorine is not included in analyses presented here due to the formation of negative ions making detection of chlorine much more difficult, which would lead to inaccurate results. The average ppb of elements detected in flint samples from the Yorkshire and Lincolnshire Wolds are presented below; the elements are presented on a series of graphs as high levels of some elements obscure the results from others (figure 7.6, 7.7, and 7.8).

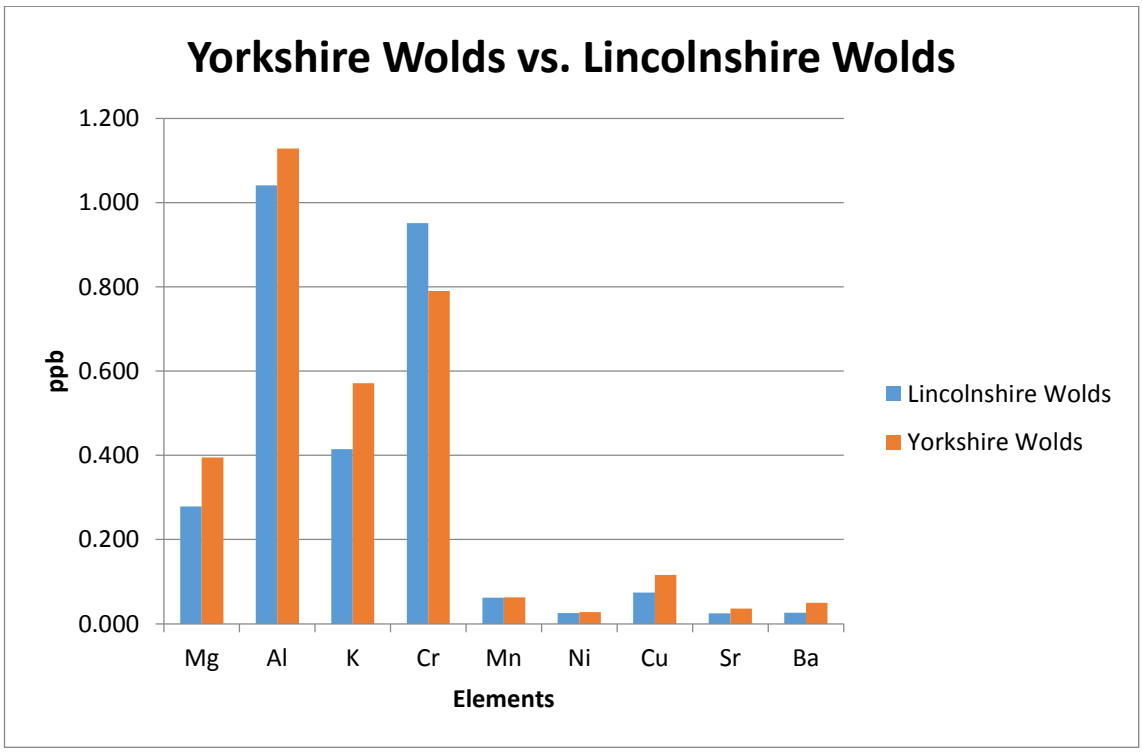


Figure 7.6 – comparison of flint samples from the Yorkshire and Lincolnshire Wolds

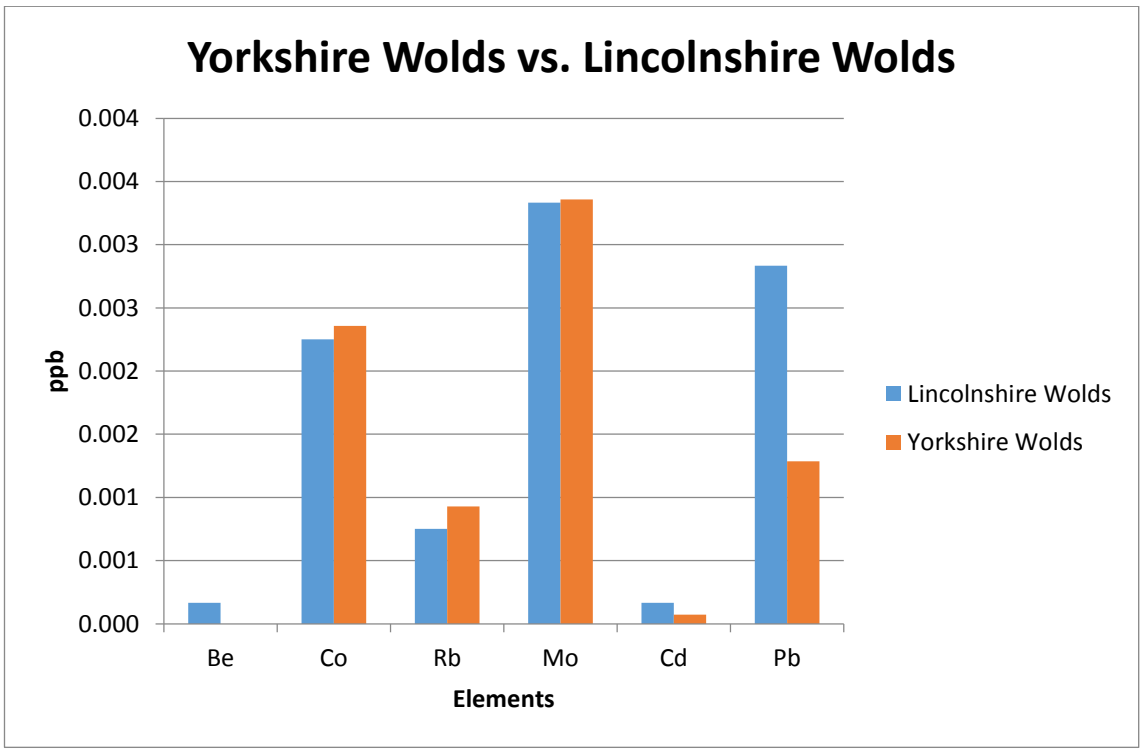


Figure 7.7 – comparison of flint samples from the Yorkshire and Lincolnshire Wolds

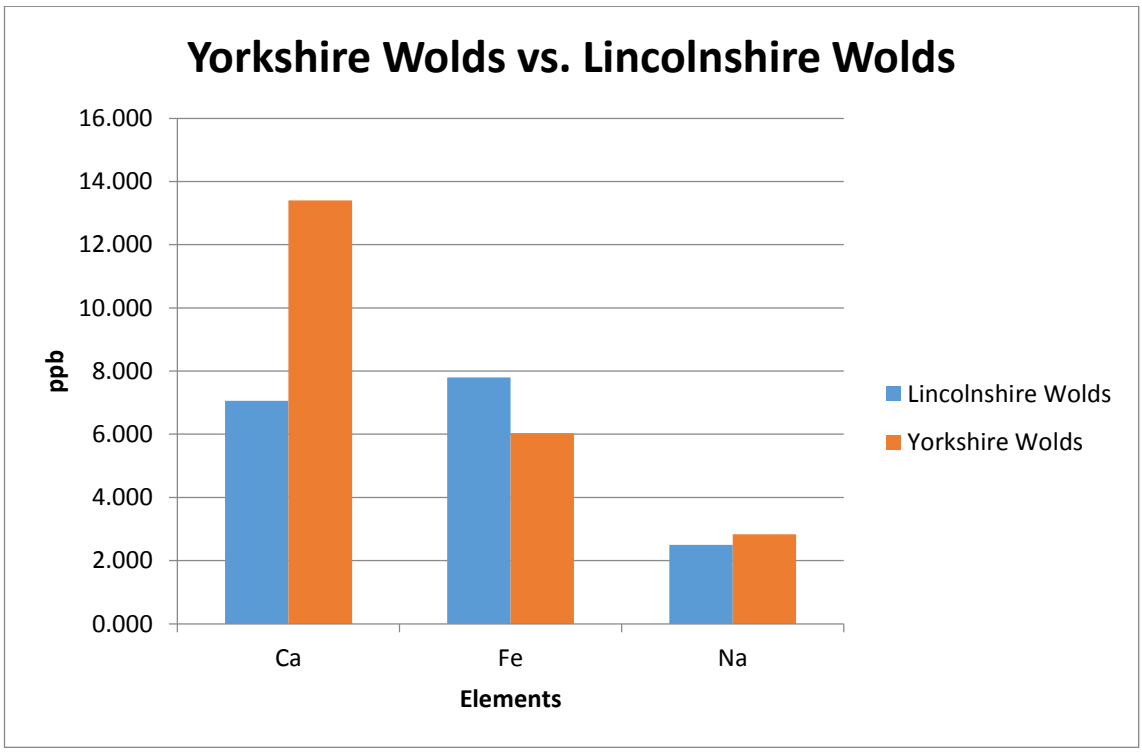


Figure 7.8 – comparison of flint samples from the Yorkshire and Lincolnshire Wolds

The differences in concentrations of two elements, iron (p=0.041) and lead (p=0.013), were statistically significant and provide a means of distinguishing between flint samples from these regions.

7.2.2 Southern Chalk province

Samples collected from nine sites in the Southern Chalk province were suitable for ICP-MS analysis: field near Pewsey, Dover coast, Cissbury, Moon's Copse, Beer, A342 Pewsey, Harrow Hill, A2 Ileden Lane, and Southwick Hill. As with the pXRF analysis, provenancing flint to discrete regions within the Southern province would be beneficial. The areas in question with regards ICP-MS samples are: Salisbury Plain/Pewsey (field near Pewsey, Moon's Copse, A342 Pewsey), South Downs (Harrow Hill, Cissbury, Southwick Hill), North Downs (A2 Ileden Lane, Dover Coast), and Southwestern Chalk (Beer). There were thirteen elements that could be

quantified from the Southern Chalk province flint samples: sodium, magnesium, aluminium, chromium, manganese, iron, cobalt, copper, rubidium, strontium, cadmium, barium, and lead.

Distinguishing the South Downs and North Downs, and South Downs and Southwestern Chalk was not possible using any of the elements listed above. None of the elements provided statistically significant *p* values. Differentiating between the North Downs and Southwestern Chalk was also not possible, with no significant *p* values recorded. Similarly, the Southwestern Chalk samples could not be distinguished from the Salisbury Plain/Pewsey samples using any of the elements above.

However, it was possible to discriminate between the samples from Salisbury Plain/Pewsey and the samples from the North Downs using the variation in lead (p=0.047).

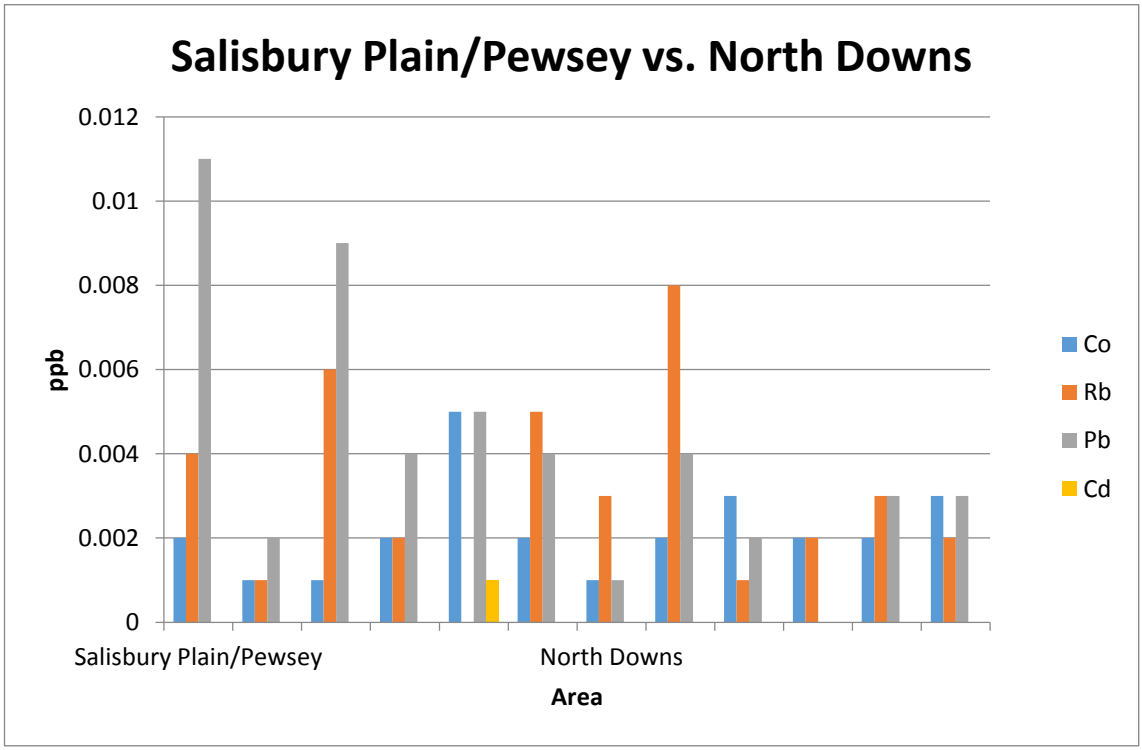


Figure 7.9 – comparison of flint samples from Salisbury Plain/Pewsey and North Downs

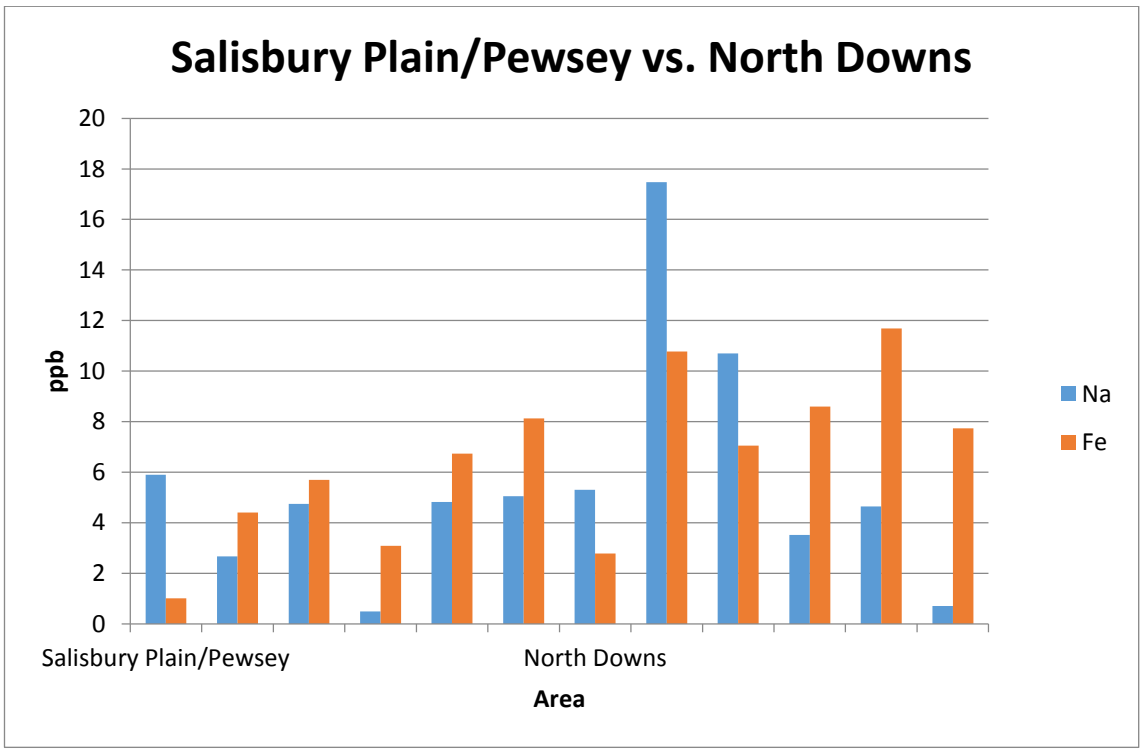


Figure 7.10 – comparison of flint samples from Salisbury Plain/Pewsey and North Downs

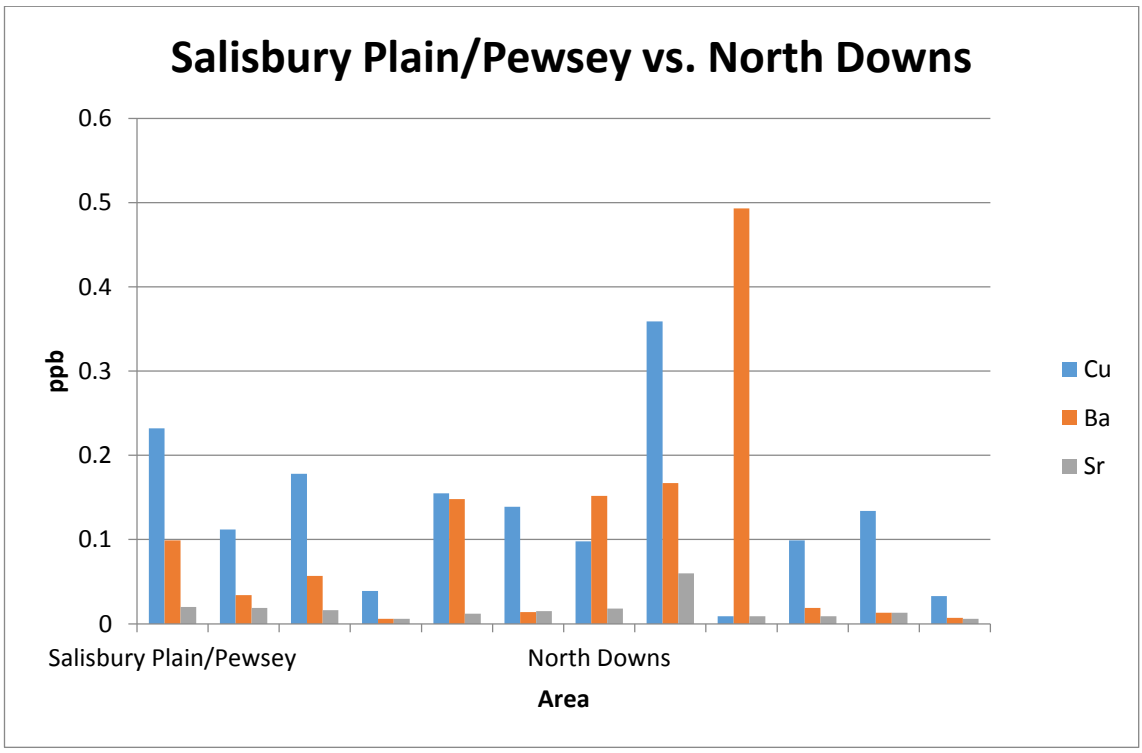


Figure 7.11 – comparison of flint samples from Salisbury Plain/Pewsey and North Downs

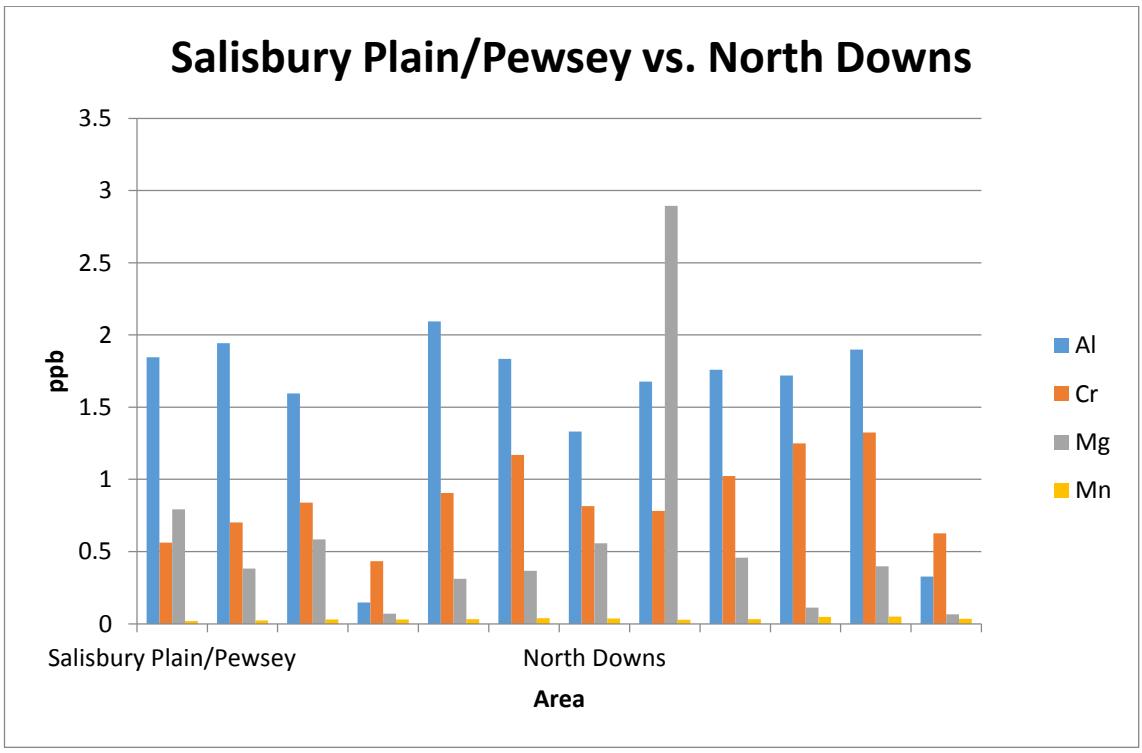


Figure 7.12 - comparison of flint samples from Salisbury Plain/Pewsey and North Downs

The South Downs samples can be differentiated from Salisbury Plain/Pewsey samples based on the variation in copper (p=0.042) (figure 7.13).

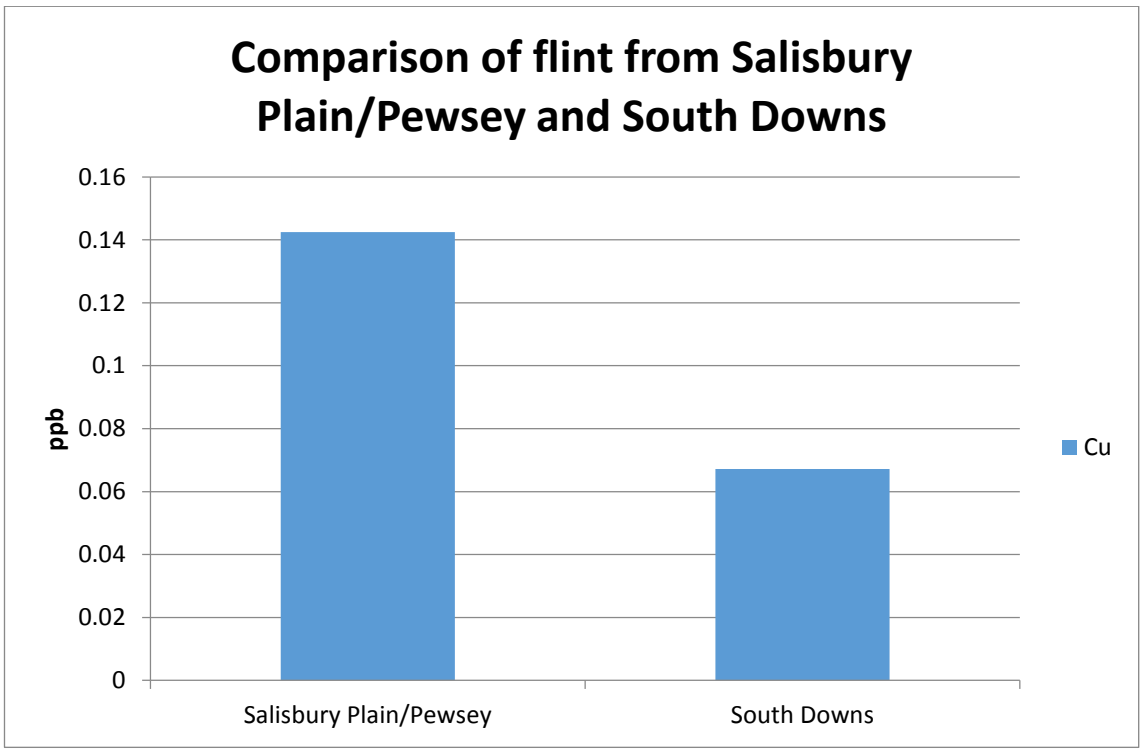


Figure 7.13 – Difference in average ppb of copper in flint samples from Salisbury Plain/Pewsey and South Downs

The ICP-MS analysis of flint samples from the Southern Chalk province provides a small number of elements that are useful for distinguishing within this large area. Lead and copper can successfully distinguish between discrete areas; however it was not possible to differentiate between the Southwestern Chalk samples and any of the other areas, indicating perhaps that this area is not geochemically distinct from the neighbouring regions.

7.2.3 Northern Ireland Chalk formation

Eight sites within the Northern Ireland Chalk formation were sampled for ICP-MS analysis: White Park Bay, Slieve Gallion, White Rocks, Carnlough, Cloughastucan, Garron Point, Ballintoy, and Portbraddan. As with the pXRF analysis, attempts were made to distinguish between the coastal and inland flint sources and between the various coastal sites.

7.2.3.1 Coastal vs. inland sources

Distinguishing between coastal and inland sources of flint in the Northern Ireland Chalk formation could be accomplished using pXRF analysis, using the variation in phosphorus, titanium, and zirconium. The results from the ICP-MS analysis indicate that differentiation between inland and coastal sources of flint can be achieved using the variation in concentrations of barium (p=0.024) and manganese (p=0.007) (figure 7.14). None of the other elements studied provided statistically significant results.

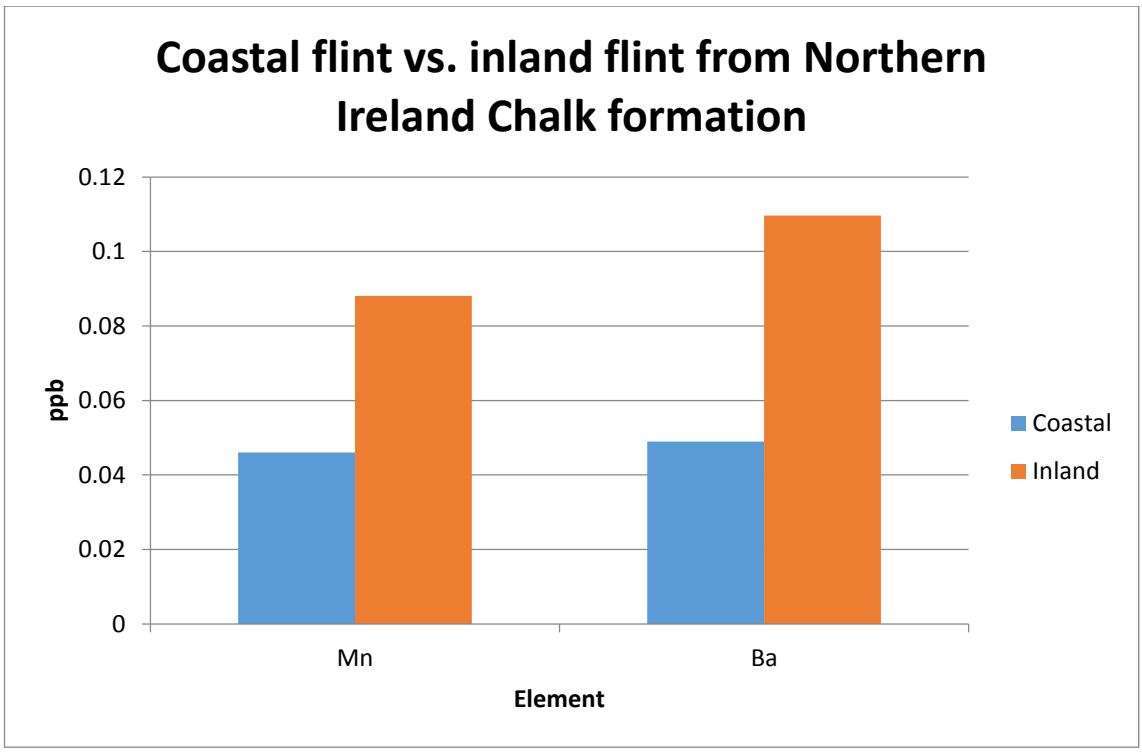


Figure 7.14 – Difference in ppb of barium and manganese detected in flint from coastal and inland sources in Northern Ireland

7.2.3.2 Between coastal sources

It was possible to distinguish between the many coastal sources of flint within the Northern Ireland Chalk formation. The pXRF analysis demonstrated that this was possible using different

elements/combinations of elements, with few exceptions. The Garron Point samples could not be distinguished from Cloughastucan, Portbraddan, or White Park Bay samples using pXRF, nor could sample from Ballintoy East and Portbraddan.

With the exception of Cloughastucan, Ballintoy East samples can be distinguished from all other sampling locations along the Antrim coast. This was not anticipated as samples collected from Garron Point can be distinguished from Ballintoy East, despite Cloughastucan and Garron Point being less than 700m apart. Ballintoy East flint samples can be distinguished from: Garron Point samples using variation in magnesium (p=0.038) and copper (p=0.007) (figure 7.15).

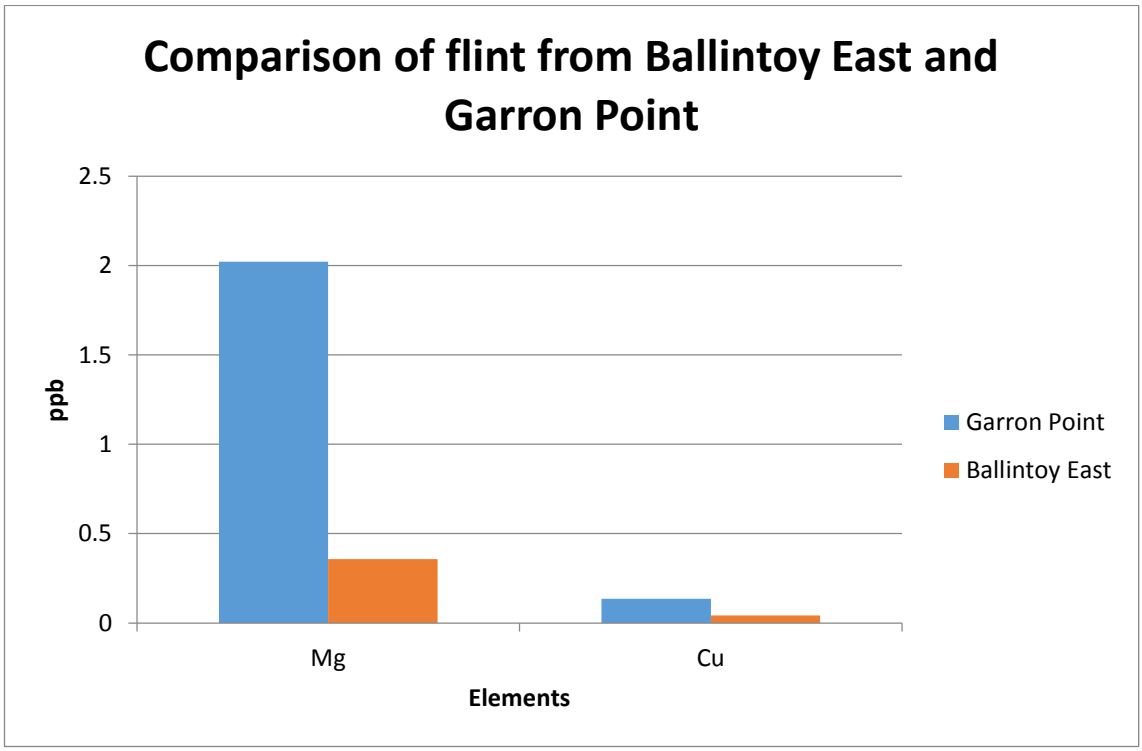


Figure 7.15 - Comparison of magnesium and copper in flint samples from Ballintoy East and Garron Point

Ballintoy East and White Rocks samples can be distinguished using strontium (p=0.006) and lead (p=0.015) (figure 7.16).

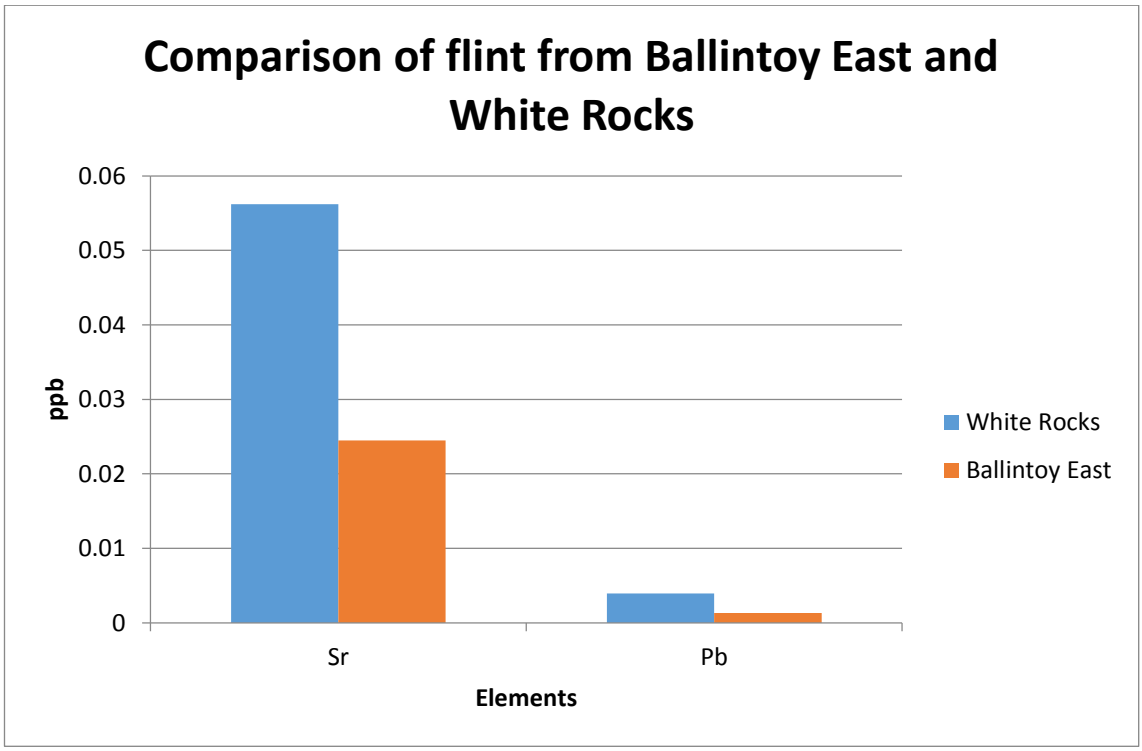


Figure 7.16 - Comparison of strontium and lead in flint samples from Ballintoy East and White Rocks

Ballintoy East samples can be differentiated from White Park Bay using magnesium (p=0.031) levels (figure 7.17); and Carnlough using cobalt (p=0.038) (figure 7.18).

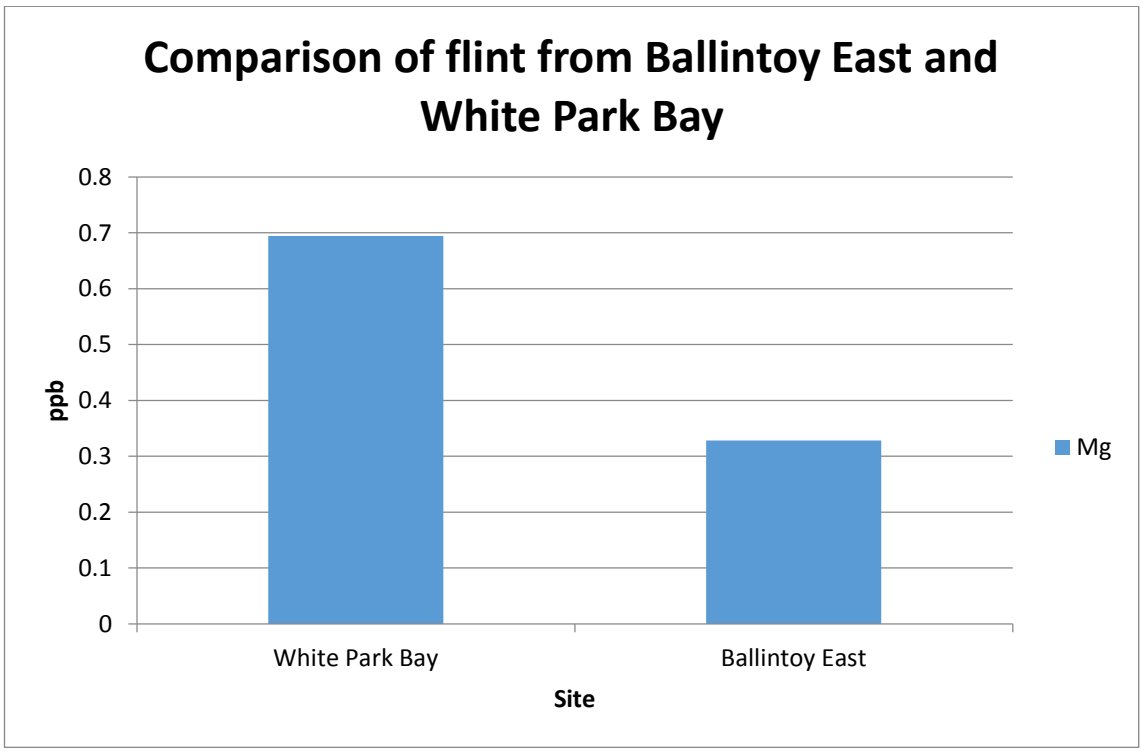


Figure 7.17 - Comparison of magnesium in flint samples from Ballintoy East and White Park Bay

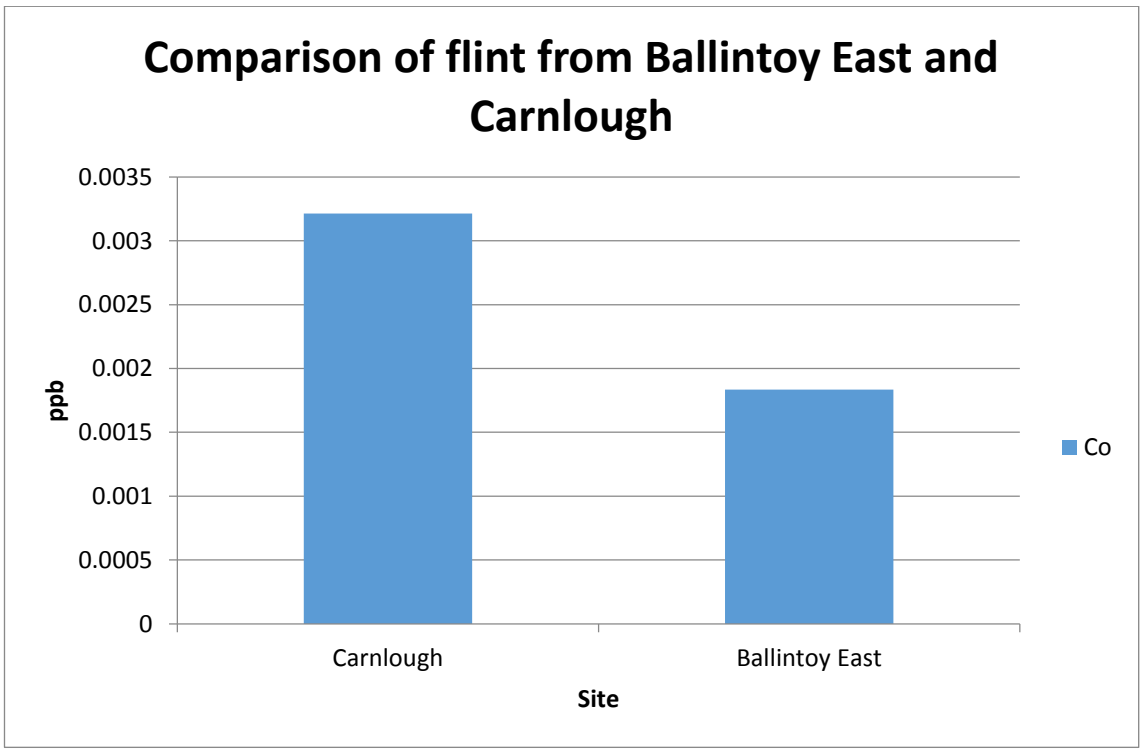


Figure 7.18 - Comparison of cobalt in flint samples from Ballintoy East and Carnlough

In addition to Ballintoy East, the samples from Garron Point can be differentiated from: White Park Bay samples using copper (p=0.017) (figure 7.19); Portbraddan samples using caesium (*p*=0.019) (figure 7.20); and from Carnlough samples using copper (*p*=0.017), chromium (*p*=0.028), and caesium (*p*=0.013) (figure 7.21).

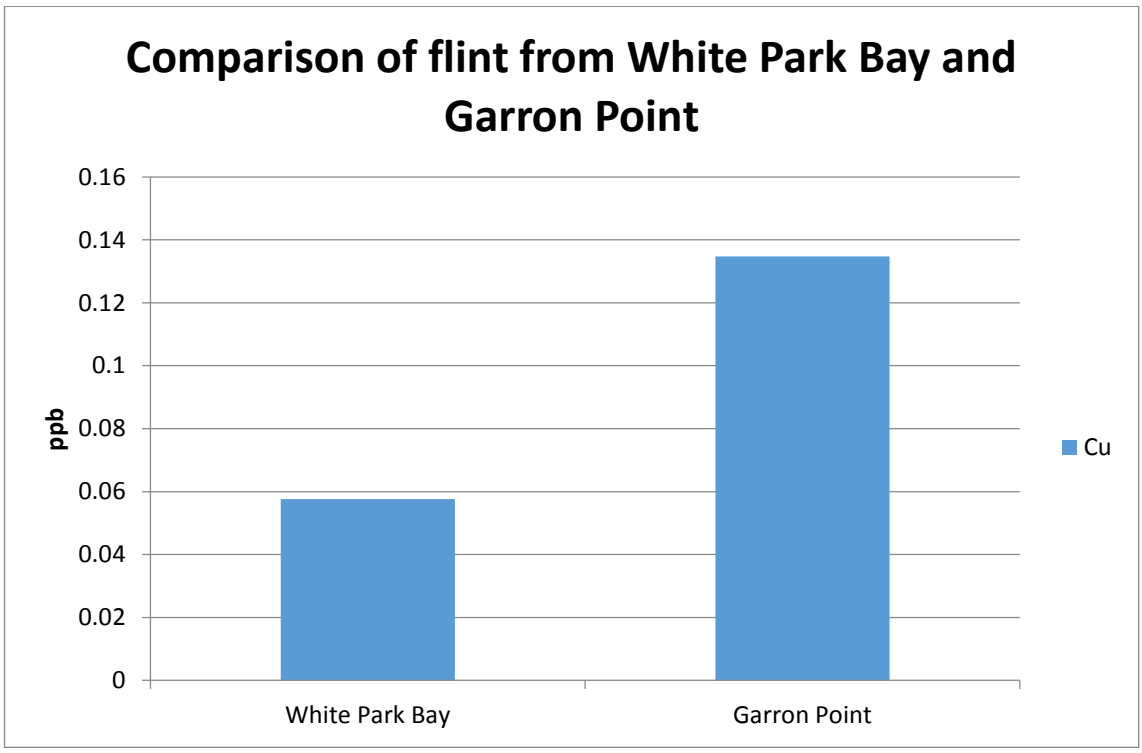


Figure 7.19 - Comparison of copper in flint samples from Garron Point and White Park Bay

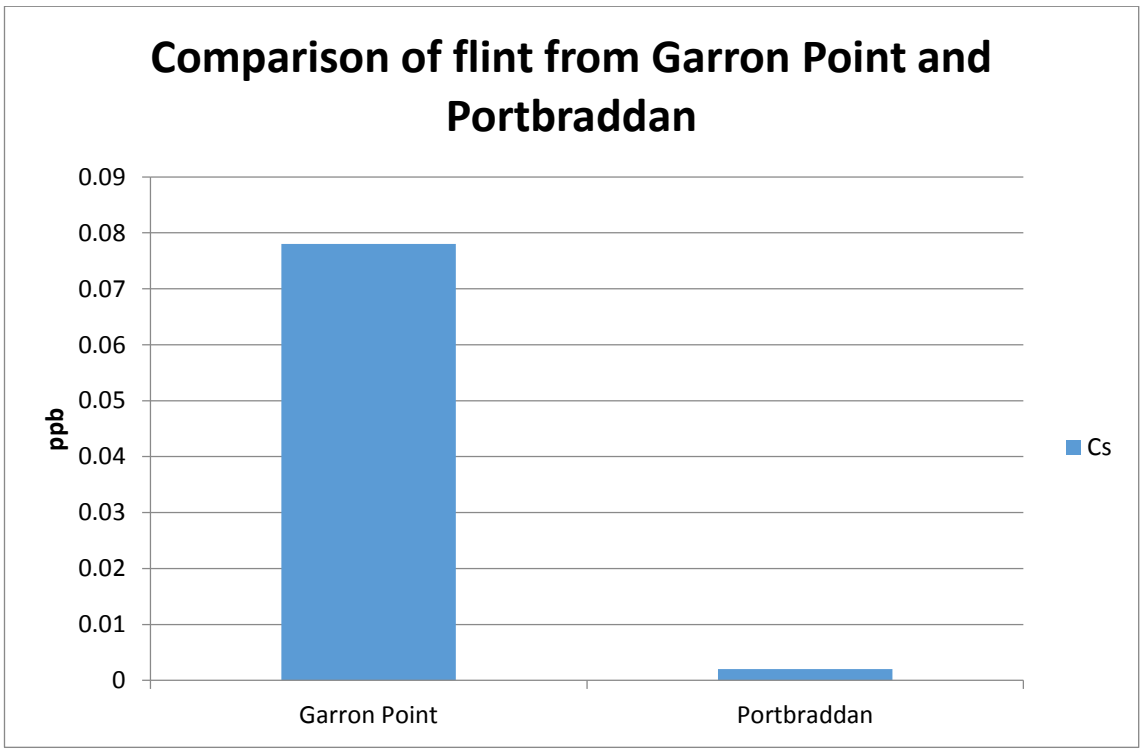


Figure 7.20 - Comparison of caesium in flint samples from Garron Point and Portbraddan

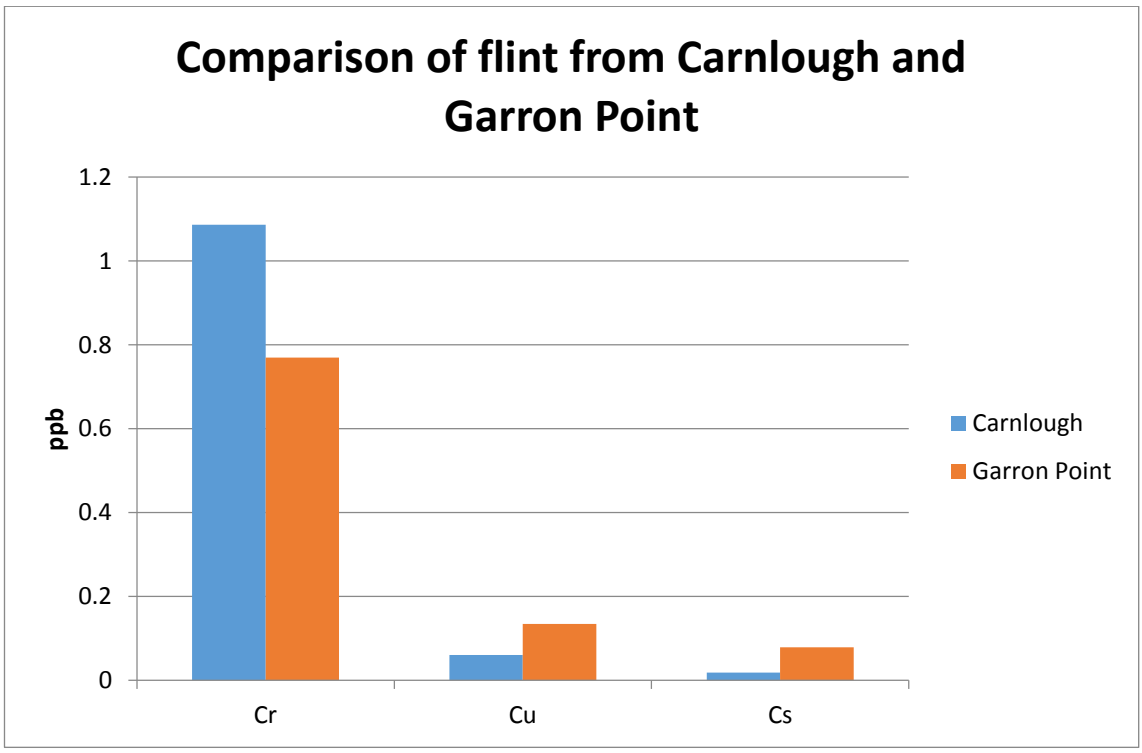


Figure 7.21 - Comparison of chromium, copper, and caesium in flint samples from Garron Point and Carnlough

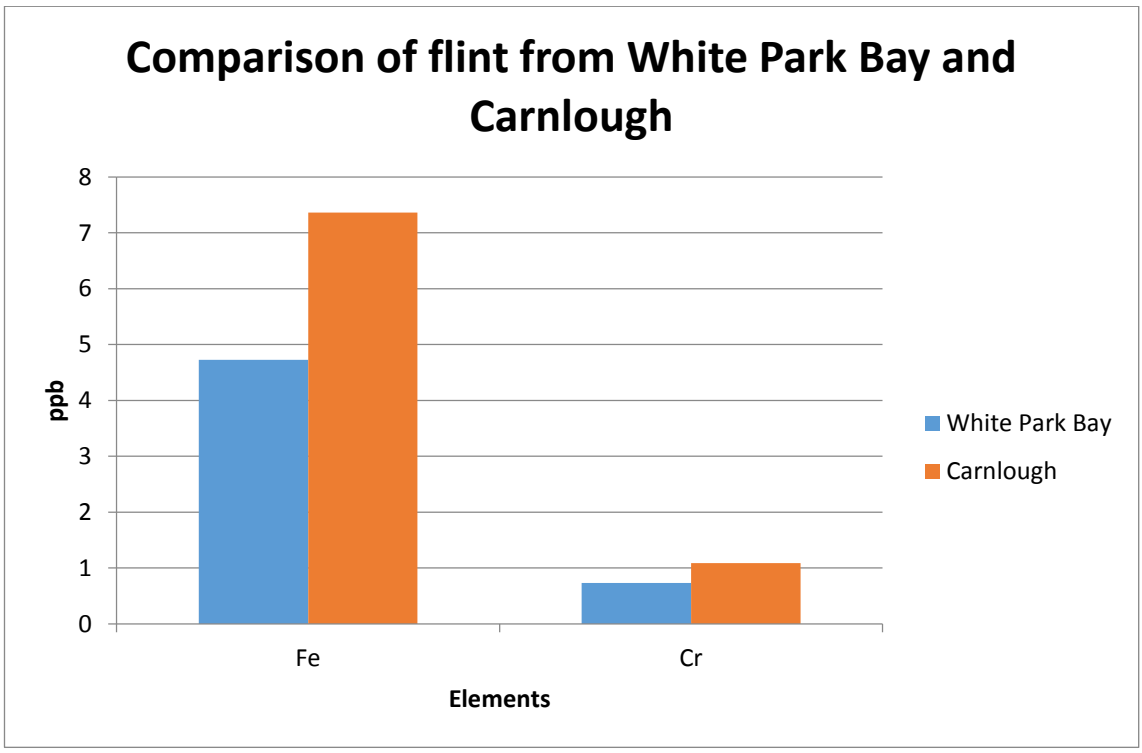


Figure 7.22 - Comparison of chromium and iron in flint samples from White Park Bay and Carnlough

Flint samples from White Park Bay can be distinguished from Ballintoy east and Garron Point (see above), and Carnlough, the latter based on variation in chromium (p=0.019) and iron (p=0.016) (figure 7.22). Carnlough flint samples can be differentiated from those collected at Portbraddan due to the variation in levels of molybdenum (p=0.036) and cobalt (p=0.041) (figure 7.23).

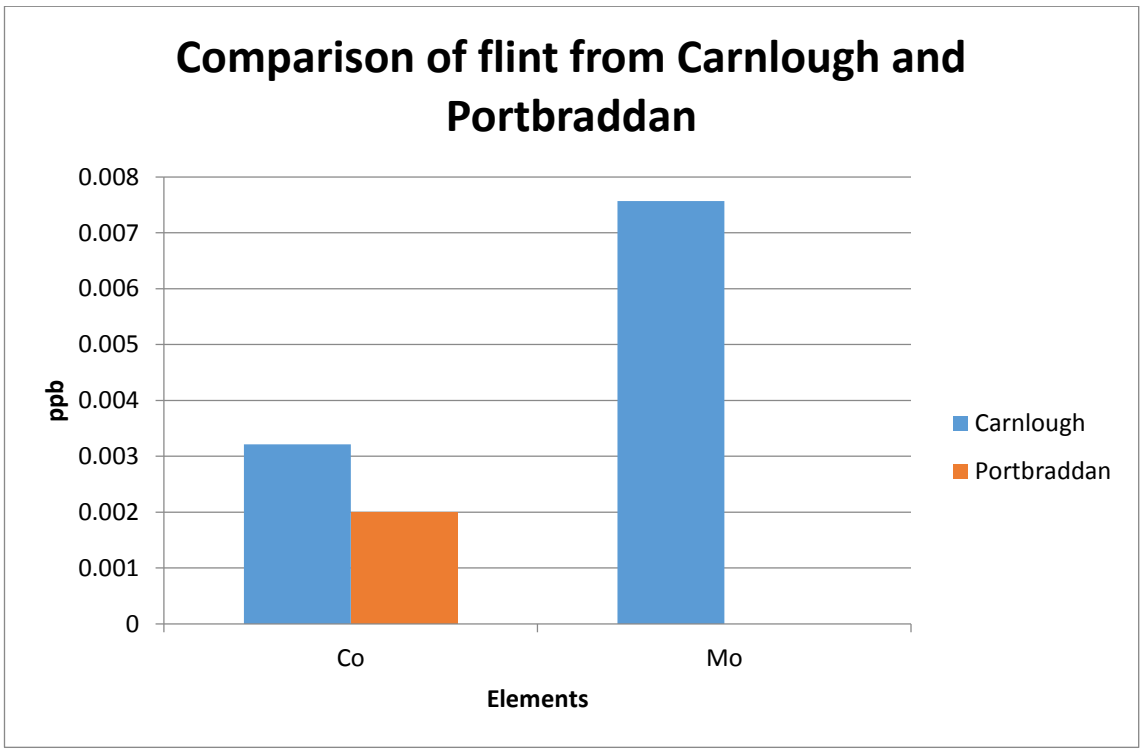


Figure 7.23 - Comparison of chromium and iron in flint samples from Portbraddan and Carnlough

It was possible to distinguish between some of coastal sites in the Northern Ireland Chalk formation using different elements/combinations of elements. Flint samples from Cloughastucan could not be distinguished from any other sites. White Park Bay and Portbraddan could not be distinguished; this is likely due to the geographic proximity of these sites. Similarly, White Rocks and White Park Bay samples could not be differentiated; although almost 14km apart they may be too geochemically similar to distinguish. The flint samples from Carnlough can be differentiated from all but two of the other locations; this may reflect the fact that Carnlough is a secondary source, with intermingled flint from an unknown range of original sources, and is likely to have greater geochemical variation as a result.

7.2.4 Differentiating chalk provinces within Britain

This section presents the ICP-MS results that demonstrate whether flint-producing Chalk provinces in Britain (Northern, Southern, and Transitional) can be distinguished using geochemical analysis.

The flint samples from the Northern and Transitional Chalk provinces can be distinguished using statistically significant variations in the concentrations of one element. ICP-MS analysis demonstrated that variation in manganese (p=0.04) provides a means of differentiating between the Northern and Transitional Chalk provinces. The pXRF analysis conducted in 6.2.5 identified five elements (chlorine, titanium, nickel, zinc, and ytterbium) that can be used to differentiate between these Chalk provinces.

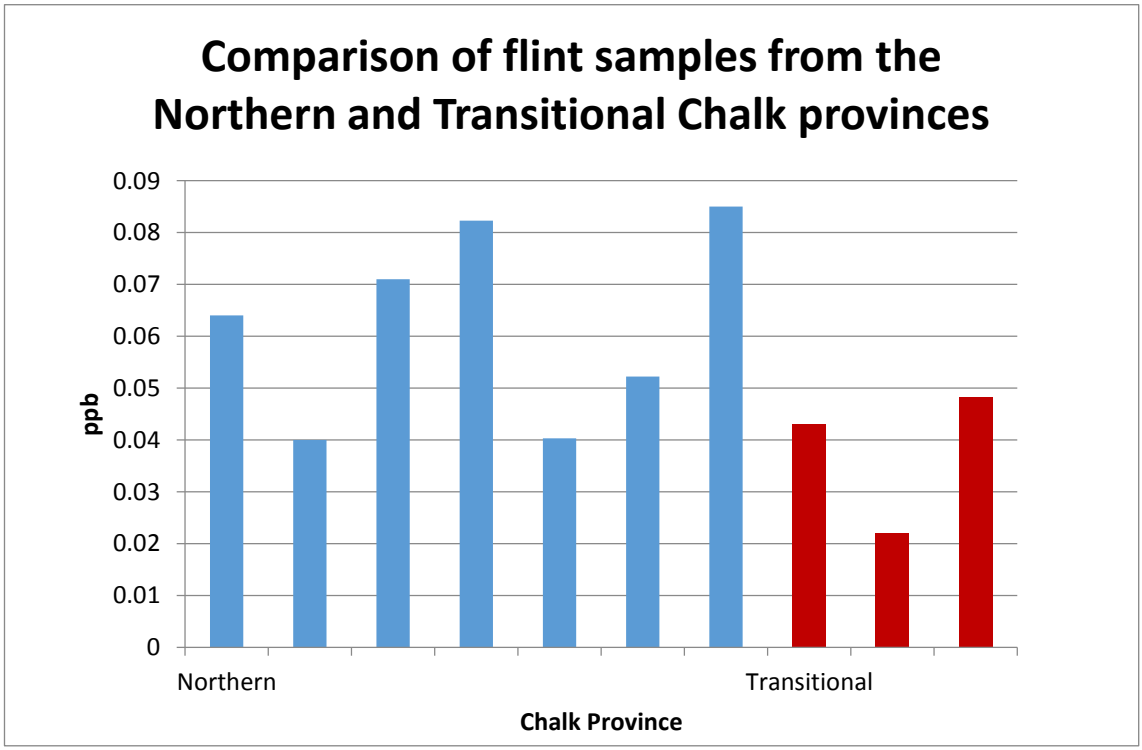


Figure 7.24 - Comparison of manganese in flint samples from Northern and Transitional Chalk provinces

The Northern and Southern Chalk provinces can be distinguished under ICP-MS analysis using one element – molybdenum (p=0.016) (figure 7.25). The pXRF analysis found that five elements provided statistically significant differences between the Northern and Southern Chalk provinces; phosphorus, chlorine, potassium, manganese, and nickel. Of these six, the variation in chlorine, potassium, and nickel were particularly significant (p=<0.0001).

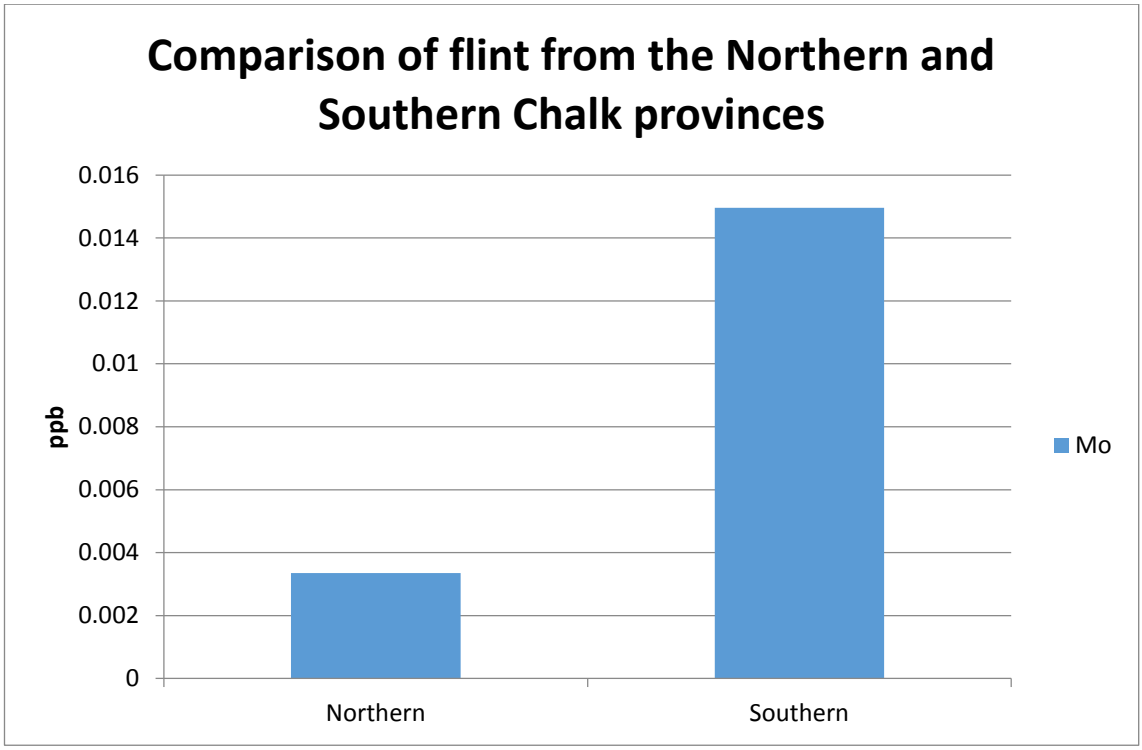


Figure 7.25 - Comparison of molybdenum in flint samples from Northern and Southern Chalk provinces

The Southern and Transitional Chalk provinces could not be distinguished using pXRF analysis, however it was possible using ICP-MS using variation in the concentration of three elements: nickel (p=0.046), copper (p=0.003), and molybdenum (p=0.02) (figure 7.26).

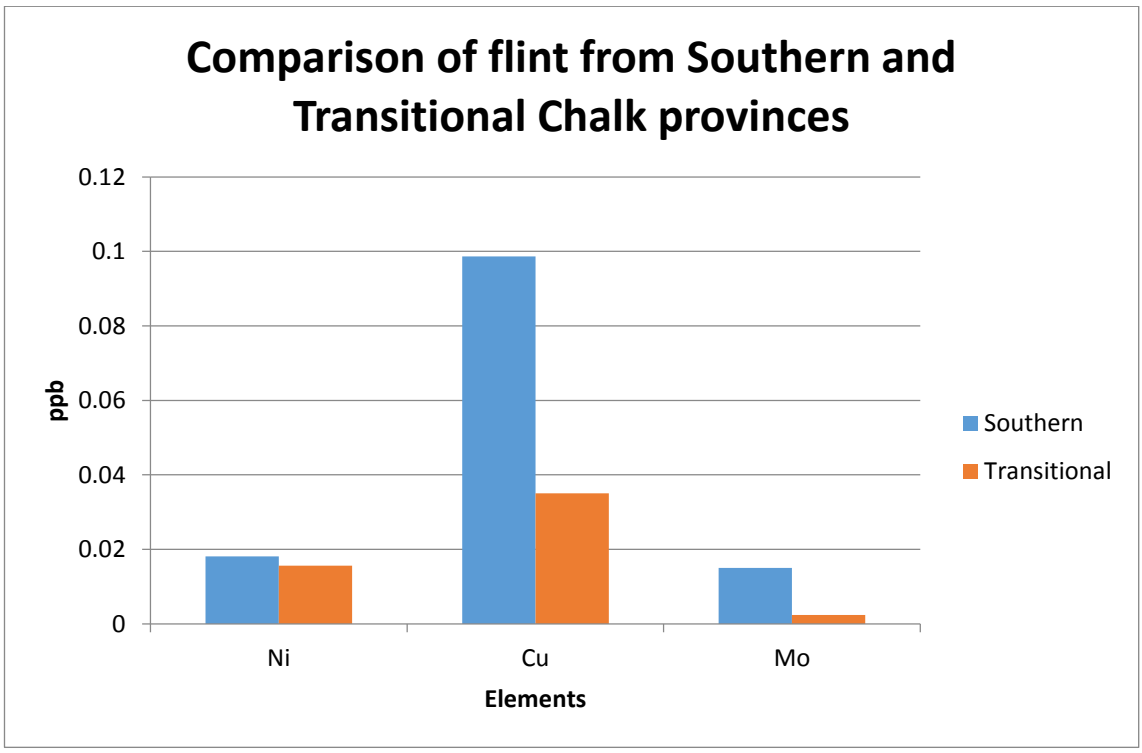


Figure 7.26 - Comparison of nickel, copper, and molybdenum in flint samples from Southern and Transitional Chalk provinces

7.2.5 Differentiating between Chalk provinces in Britain and Ireland

The pXRF analysis conducted in 6.2.6 found that flint samples from Ireland and flint samples from Chalk provinces in England can be distinguished using variation in the relative percentages of two elements: chlorine and cobalt. The ICP-MS analysis found that the concentration of three elements varies in statistically significant way: magnesium (p=0.015), aluminium (p=0.001), and molybdenum (p=0.009) (figure 7.27).

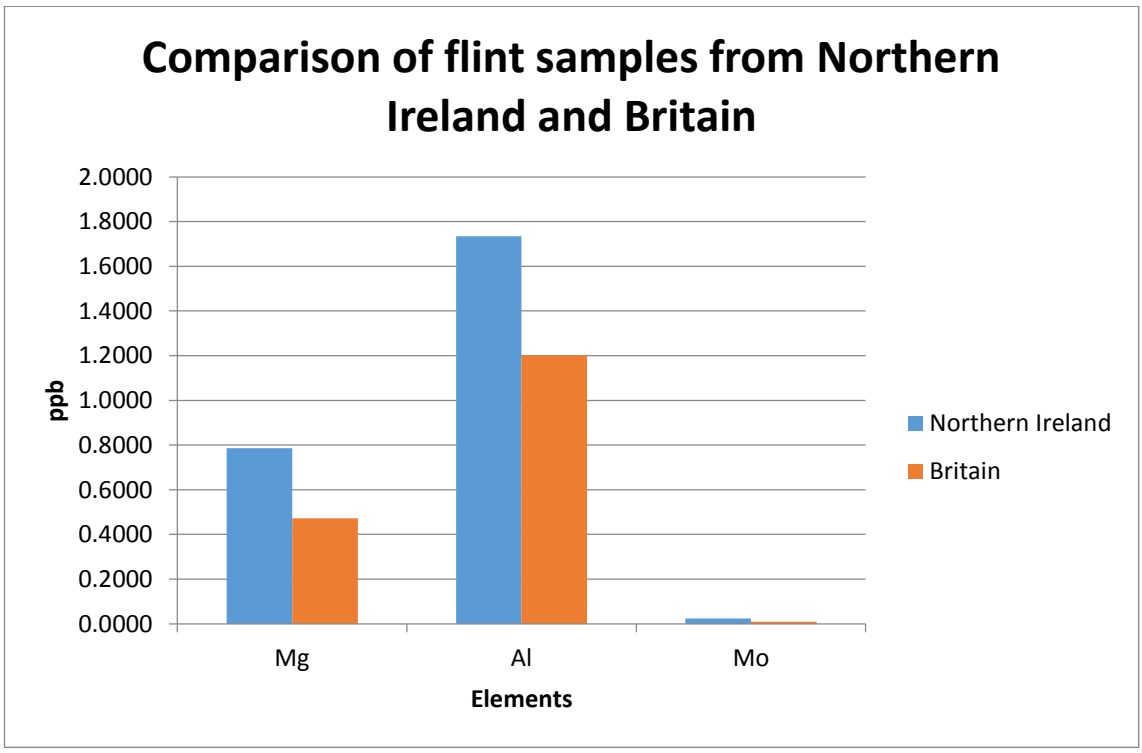


Figure 7.27 - Comparison of magnesium, aluminium, and molybdenum in flint samples from Northern Ireland and Britain

7.2.6 Comparison with previous studies

Two previous studies have utilised ICP-MS analyses to investigate geochemical provenancing of flint within Britain and found that sources of flint can be differentiated (Rockman 2003; Pettitt *et. al.* 2012). The ICP-MS analysis conducted by Rockman found that flint from the South Downs can be distinguished from Transitional province flint samples based on the concentration of rubidium, however the current study found that separating Southern Chalk province flint from Transitional province flint can be achieved using variation in the concentrations of nickel, copper, and molybdenum. Pettitt *et. al.* (2012) used LA-ICP-MS to investigate movement of raw material within Britain and demonstrated that the most useful elements for differentiating between the Northern, Southern, and Transitional provinces were

aluminium, potassium, rubidium, zirconium, niobium, and barium (Paul Pettitt *pers. comm.*). The results outlined in this chapter do not corroborate these findings as the elements useful for differentiation of Northern/Southern/Transitional provinces in this study are molybdenum, manganese, nickel, and copper.

Previous provenancing studies have identified aluminium as being of particular importance for provenancing flint from Britain (Sieveking *et. al.* 1970; Sieveking *et. al.* 1972; Durst 2009). That was not the case here; statistically significant variation in aluminium concentration only occurs when comparing samples from Northern Ireland and samples from Britain.

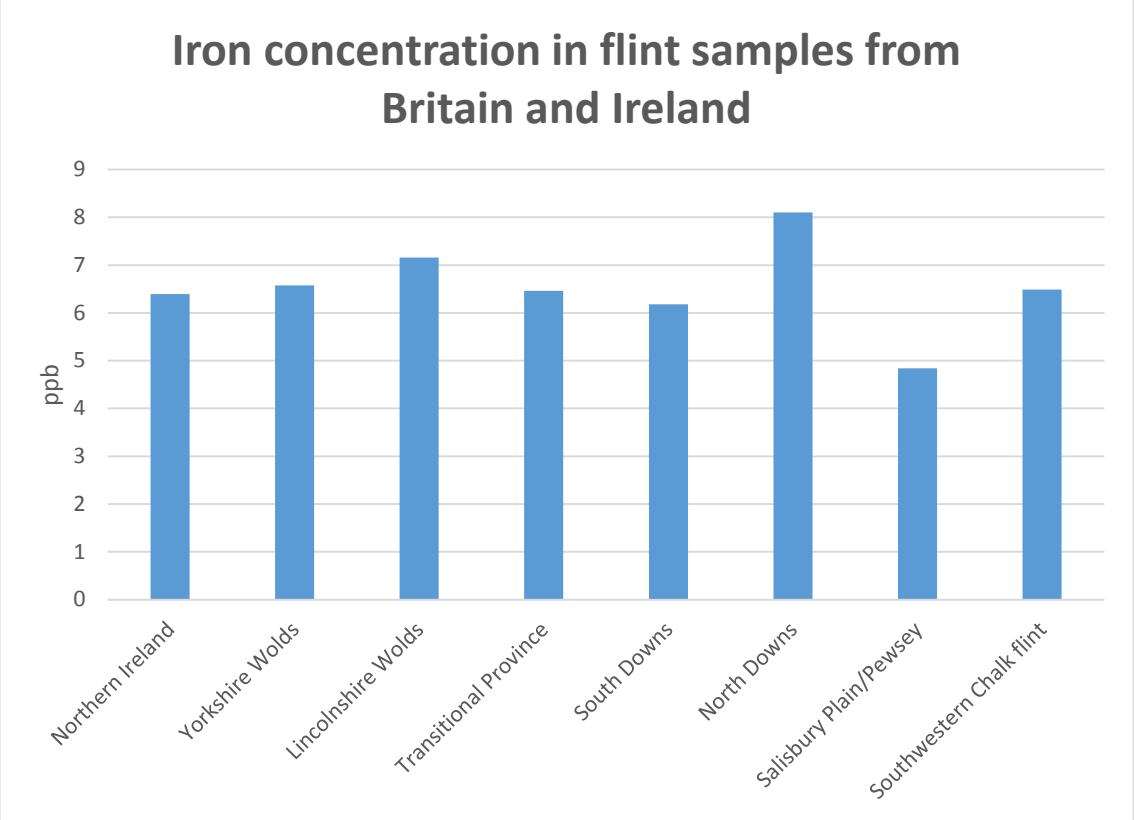


Figure 7.28 – Comparison of average iron concentration from samples collected from major flint-producing areas within Britain and Ireland

One of the distinguishing features of flint from the Southwestern chalk identified by Sieveking *et. al.* 1972 was the comparatively high concentration of iron. Figure 7.28 above demonstrates that the Southwestern chalk flint analysed using ICP-MS does not contain a particularly noteworthy concentration of iron, and was in fact surpassed by samples collected from the Lincolnshire Wolds and the North Downs.

The analysis conducted by Sieveking *et. al.* (1972) shares some sites (Grime's Graves, Cissbury, and Beer) and elements (aluminium, iron, magnesium, potassium, and sodium) in common with the ICP-MS analysis conducted in this thesis (table 7.1).

	Sieveking *et. al.* 1972		**Current study**	
	Most abundant	**Least abundant**	**Most abundant**	**Least abundant**
Grime's Graves	Aluminium	Magnesium	Iron	Magnesium
Cissbury	Aluminium	Magnesium	Potassium	Magnesium
Beer	Aluminium	Magnesium	Potassium	Magnesium

Table 7.1 – comparison of most/least abundant elements in shared sites and elements from Sieveking *et. al.* 1972 and the current study

Immediately obvious are the consistently low concentrations of magnesium quantified from these sites, and the predominance of aluminium in the samples analysed in 1972. The methods used by Sieveking *et. al.* (1972) differ from the instrumentation used here, however as was demonstrated in the work of Rockman (2003) different methods may not be directly comparable but the patterns in the data can be evaluated. In this sense, it is interesting that both methods show magnesium as the least abundant element. It is difficult to give a more

detailed comparison as so few sites and elements are shared by both Sieveking *et. al.* and the current study.

The results published by Aspinall & Feather (1972) also share some sites (Cissbury and Grime's Graves) and elements (caesium and chromium) with the current study. Comparison of the results is outlined below (table 7.2).

	Aspinall & Feather 1972		**Current study**	
	Caesium	**Chromium**	**Caesium**	**Chromium**
Cissbury	0.013	0.6	0.000214	0.0009458
Grime's Graves	0.023	0.7	0.000001	0.00598

Table 7.2 – comparison of caesium and chromium mean concentration (ppm) in flint samples from Cissbury and Grime's Graves

Broadly speaking, the data in table 7.2 shows agreement between Aspinall & Feather (1972) and this study in relation to the concentration of caesium and chromium. Both studies show that chromium is more abundant in samples from both Cissbury and Grime's Graves.

7.3 ICP-MS results conclusion

Analysis of flint samples using ICP-MS was conducted to determine whether flint from different Chalk provinces within Britain and Ireland can be distinguished on a geochemical basis, and whether the presence of patina impedes analysis.

From the ICP-MS results outlined above, patinated surfaces do not appear to have as great an effect on geochemical provenancing as was found with pXRF analysis. The samples from the Northern Ireland Chalk formation show no statistically significant variation between patinated

and unpatinated flint, however patinated samples from the Southern Chalk province display significant variation in the concentration of chromium.

The Chalk provinces in Britain can be distinguished using different elements/combinations of elements. Flint samples from the Northern and Southern provinces can be differentiated using variation of one element (molybdenum), as can the Northern and Transitional provinces using manganese. It was possible to distinguish the Southern and Transitional provinces using ICP-MS based on the difference in nickel, copper, and molybdenum concentrations within these areas. The Chalk provinces in Britain contain smaller geographic regions that were investigated to determine if they can be differentiated on the basis of their geochemistry. Within the Northern province, the Yorkshire and Lincolnshire Wolds can be distinguished using varying concentrations of lead and iron. The areas within the Southern province – North Downs, South Downs, Southwestern Chalk, and Salisbury Plain/Pewsey – can be distinguished using a small number of elements; copper, lead, and manganese.

The ICP-MS analysis found that it was possible to differentiate between flint samples from Britain and samples from Ireland using variation in the concentrations of four elements: beryllium, magnesium, aluminium, and molybdenum.

Samples from the Northern Ireland Chalk formation were mainly from coastal locations, with one inland locale. Distinguishing between coastal and inland sources could be achieved using ICP-MS through variation in barium and manganese concentrations.

This chapter has outlined the results of the ICP-MS analysis of flint samples from within the study area and found that it is possible to distinguish between Britain and Ireland, as well as between discrete regions within (with some exceptions). The presence of patina does not

appear to seriously impede analysis, but as with the pXRF results, there are indications that the effect of patina is not constant across the Chalk provinces and needs further consideration.

8.0 ARTEFACT CASE STUDIES

The results outlined in Chapter 6 demonstrated the application of pXRF in terms of recognising primary sources of flint within Britain and Ireland. However, one of the stated aims of this research was to investigate the ability of geochemical sourcing in terms of provenancing actual archaeological artefacts. This is crucial, as the ability to provenance archaeological artefacts will greatly enhance our knowledge of movement, trade, and procurement of raw material during prehistory. The following chapter will present a number of case studies from flint tool assemblages collected from within the study area and from a variety of prehistoric periods as well as two blind sample tests. The investigations outlined in this chapter should be regarded as a pilot study to gauge the efficacy of this approach, and to identify areas for improvement in future analyses. Full details of statistical analysis are contained in appendix 8.1.

8.1 Artefact assemblages

Five artefact assemblages were analysed using pXRF: Kintyre, Threefords, N1F recollection, Nether Exe, and Bann Valley (figure 8.1).

Figure 8.1 – Locations of artefact assemblages

8.1.1 Kintyre artefacts

A total of 51 artefacts and pieces of flint from southern Kintyre were analysed using pXRF (appendix 8.2). This assemblage was collected during fieldwalking exercises (figure 8.2) conducted as part of the Southern Kintyre Project (Cummings & Robinson 2015), and was made available by Dr Vicki Cummings, University of Central Lancashire.

Figure 8.2 – Study area, Southern Kintyre Project, showing proximity to Northern Ireland (Tableau software © 2016)

The assemblage is predominantly Mesolithic and Bronze Age, with a small number of Neolithic pieces. Diagnostic artefacts include late Neolithic/early Bronze Age barbed-and-tanged arrowheads, and early Bronze Age thumbnail scrapers. The majority of artefacts are either grey in colour or have an orange/brown patina.

There are no chalk outcrops in the area, the nearest primary sources of flint are located on the Antrim coast across the Irish Sea, or the chalk outcrops along the coast of East Yorkshire. However, the lack of chalk outcrops does not equate to lack of flint; there are numerous deposits of flint pebbles on beaches (including in the Kintyre area), as well as river gravels, raised beaches, and gravel deposits of flint nodules (Wickham-Jones 1986, 1-2). The flint

industry excavated from the Mesolithic site at Auchareoch (located on the Isle of Arran near the southern tip of Kintyre) has cortex remaining of 12% of the assemblage, the appearance of which indicates it most likely came from local beach sources (Affleck *et. al.* 1988, 46). It is anticipated that the raw material for the Kintyre artefact assemblage investigated here will be primarily beach flint, the likeliest source for the majority of flint in this area (Mithen 2015, 333). Beach flint has the potential to provide a great deal of difficulty when attempting to provenance as the flint may have been weathered from a variety of sources spread over a large geographic area. Some of these sources may be underwater or may no longer exist, making it impossible to provenance accurately.

A portion of this assemblage (#1-22) has previously been analysed using pXRF to investigate provenance (Cummings & Bradley 2015), however this was conducted prior to Northern province samples being available for comparison. This analysis found that most artefacts were likely to have been made on beach pebbles local to Kintyre. The current study will investigate this further.

8.1.2 Threefords artefacts

Twenty artefacts and pieces of struck flint from Threefords, Northumbria (figure 8.3), were analysed using pXRF. The Threefords site is located in the Milfield Basin, Northumberland, an area with great archaeological significance due to the Neolithic enclosures and henges, and Early Bronze Age funerary monuments (Edwards 2004, 59). The nearby site of Thirlings revealed extensive Neolithic pit and post-pit features, with substantial amounts of early and later Neolithic pottery recovered (Miket *et. al.* 2008).

These artefacts were recovered from an atypical early Neolithic house and midden, and the majority are made from dark grey flint, although some pieces are mottled brown/orange

(appendix 8.2), and were obtained for the current analysis by Dr. Seren Griffiths (University of Central Lancashire). The site dates to approximately 38-37th century cal. BC. (Griffiths *pers.comm*). Artefacts include blades, flakes, and scrapers.

Figure 8.3 – Location of Threefords site within the north of England (Tableau Software © 2016)

The closest primary source of flint to the site are the chalk outcrops on the coast of East Yorkshire. However, there is an abundance of pebble flint on beaches on the northeast coast of England (Waddington *et. al.* 2003, 8). The raw material used to create the Threefords artefacts analysed here may have come from these local beach sources, have been imported from further afield, or a mixture of raw material sources may have been used.

8.1.3 Nether Exe enclosure and N1F recollection

Two collections from the south of England were provided by Dr. Olaf Bayer (University of Oxford). As part of his PhD research (2011), Bayer conducted a systematic fieldwalking exercise around Nether Exe, a probable early Neolithic enclosure in Devon (figure 8.4).

Figure 8.4 – Location of Nether Exe and N1F recollection in Devon (Tableau software © 2016)

Twenty artefacts and struck pieces from Nether Exe were analysed (appendix 8.2). The majority of pieces are made from dark grey flint, although there are also a number of artefacts made from light grey flint. Bayer also conducted a fieldwalking exercise over an area where a non-systematic survey had been conducted previously - referred to as N1F recollection in his thesis. The artefacts in the N1F recollection are broadly Neolithic and later in date (Bayer 2011, 267); 34 of these were analysed using pXRF (appendix 8.2). Similar to the Nether Exe assemblage, the N1F recollection assemblage is made from dark grey and light grey flint. The assemblages collected by Bayer during this study were predominantly made from nodular flint

(over 90%), although there were a smaller amount of artefacts made from pebble flint (Bayer 2011, 219). Within the assemblages he collected, Bayer noted that the chronologically diagnostic artefacts from the Early Neolithic onwards were made almost entirely of flint (Bayer 2011, 223).

Due to the proximity of the Southwestern Chalk formation along the southern coast of Devon (approximately 30km), it was hypothesised by Bayer that the dark grey flint was being transported from the flint-rich outcrops around Seaton (Olaf Bayer *pers. comm.*). The current analysis will determine if this is the case, or if flint is being sourced from further afield.

8.1.4 Bann Valley artefacts

The first assemblage is a collection of artefacts and struck pieces (appendix 8.2) recovered during a series of fieldwalking exercises conducted by the author in 2006/7, from two fields bordering the River Bann approximately 2.4km southeast of Kilrea, Co. Derry (figure 8.5). The broad valley of the Lower River Bann, stretching between Lough Neagh and the north coast of Co. Derry is well-known in studies of the Irish Mesolithic due to the abundance of artefactual remains (Woodman 2015, 59) and the discovery of evidence for Mesolithic settlement at Mount Sandel (Upper and Lower), Castleroe, and Newferry (O'Kelly 1989, 19). The importance of the Bann Valley in Irish Mesolithic studies is also attested to by the term 'Bann flake', describing the large, butt-trimmed tools found in large numbers in this area. The importance of the Bann Valley, and indeed northeast Ireland, has been attributed to the availability of flint along the Antrim coast (Woodman 1978, 208), however this view has since been abandoned, along with suggestions that the earliest settlement of Ireland was confined to the northeast of Antrim (Woodman 2015, 62). The predominance of the Bann Valley in Irish Mesolithic studies is largely due to the focus of research and excavation in this part of Ireland. Commercial

exploitation of the River Bann and strong traditions of amateur artefact collection produced huge amounts of material that dominates our view of the Irish Mesolithic (see Woodman *et. al.* 2006).

In total, 57 artefacts and pieces of struck flint were analysed using pXRF. The diagnostic artefacts within this assemblage indicate a chronological range from the early Mesolithic to Neolithic. This assemblage was recovered from a field that is regularly ploughed, and may represent the remains of periods of occupation on the site during prehistory. An early Mesolithic microburin and a broken flaked axe were recovered; the late Mesolithic is represented in this assemblage by four complete Bann flakes, and two incomplete butt-trimmed pieces. A small knife, with fine retouching along both edges, and two scrapers, represent the Neolithic period.

Of particular interest within this assemblage are a collection of small blades, made from light grey flint, all found in a discrete area (approximately $3m^2$, location indicated by star on figure 8.4). Fourteen of the blades were sampled for pXRF analysis; the remainder did not meet the minimum size requirements ($1cm^2$ surface for analysis, 3mm thickness). As well as the blades, this area contained a microburin made from light grey flint, also sampled. The presence of light grey flint is unusual as the majority of artefacts from this location have a dark orange/brown patina. Another significant find is a large, orange/brown flake from a flint beach cobble with impressions of a sea urchin fossil on the exterior surface.

Figure 8.5 – Sample collection area, Bann Valley artefacts (Tableau software © 2016)

The sample collection area is approximately 30km from the nearest primary source of flint on the north coast of Antrim, although smaller flint cobbles occur in glacial till across the majority of Ireland (Briggs 1986, 186). The presence of flint with a sea urchin fossil impression could represent preferential selection of raw material with unusual characteristics or features.

The source of the raw material from which these artefacts were made is, of course, unknown, however it is not out of place here to suggest that the likeliest source of flint would be the glacial till covering the majority of the country, or the flint-rich chalk outcrops on the northern and eastern coast of Antrim. Long-distance movement of flint is implied at the late Mesolithic site at Foley Cave, Co. Cork, as flint blades found there are of a size inconsistent with the meagre flint sources in the south of Ireland (Dowd 2015, 88). It has also been suggested that the flint industry excavated from Dalkey Island, Co. Dublin, made use of imported chalk flint from Antrim due to the discovery of a nodule with chalky cortex, in contradiction with the

beach pebbles found in the area (Briggs 1986, 188). Importation of flint is also evidenced at Mount Sandel Lower, the cortex of artefacts indicating the use of both freshly quarried chalk flint and chattered beach pebbles (Collins 1983, 6-7), and at Newferry where the quality of the flint used indicates it was being brought from the coast instead of using the locally available pebbles (Woodman & Anderson 1990, 382-3). Against this backdrop, the Bann Valley assemblage under investigation here could have been made from flint imported from the coast, or at least from a source much further afield than the immediate area.

8.2 Provenancing

Discriminant function analysis was conducted to determine provenance of the various artefact assemblages. The following analysis presumes that the raw material used in the artefact assemblages could have been collected from any source(s) of flint within Ireland or Britain. It is acknowledged that the raw material may have been collected from sources of flint that have not been sampled during this study, or from outside of Ireland and Britain; exact provenancing relies on a knowledge of all potential primary and secondary sources, which is not often the case (Harding *et. al.* 2004, 78).

The pXRF results obtained from these artefactual assemblages were compared to the results obtained from flint samples collected from the entire study area. The assemblages and flint samples were analysed under the same conditions and using the same instrumental settings. All of the flint samples collected from Britain and Ireland make up the discriminant function groups as outlined below.

The flint sampling regions were split into three groups: Northern Chalk province, Southern Chalk province (incorporating the Transitional Chalk province), and Northern Ireland Chalk. This separation obtained the highest overall classification accuracy (table 8.1). Other groupings were considered but did not achieve higher classification accuracy: attempting maximum separation of sample collection areas (nine group separation of Yorkshire Wolds, Lincolnshire Wolds, Yorkshire Chalk, Transitional Province, North/South Downs, Salisbury Plain/Pewsey, Southwestern Chalk, inland Northern Ireland, and coastal Northern Ireland) resulted in a classification accuracy of 51.6%. Merging some of these groups into larger geographic areas resulted in the classification accuracy stated above (79.1%).

As there were three groups under analysis here, two discriminant functions were produced. The first function explains 93.1% of the variation between the groups and has an Eigenvalue of 3.142, indicating a strong discriminating ability. The Wilk's lambda scores indicate that the group means do differ and that these differences are statistically significant (*p* values for both <0.01). In both discriminant functions zirconium provides the strongest method of discriminating between the three groups, lutetium and cobalt are the second most effective in the first and second discriminant functions respectively.

The group centroids on figure 8.6 show the mean values of each group of samples. For provenancing purposes, discriminant function analysis will sort ungrouped cases (readings from artefacts) into the pre-established groups (figure 8.6) to which they are most similar.

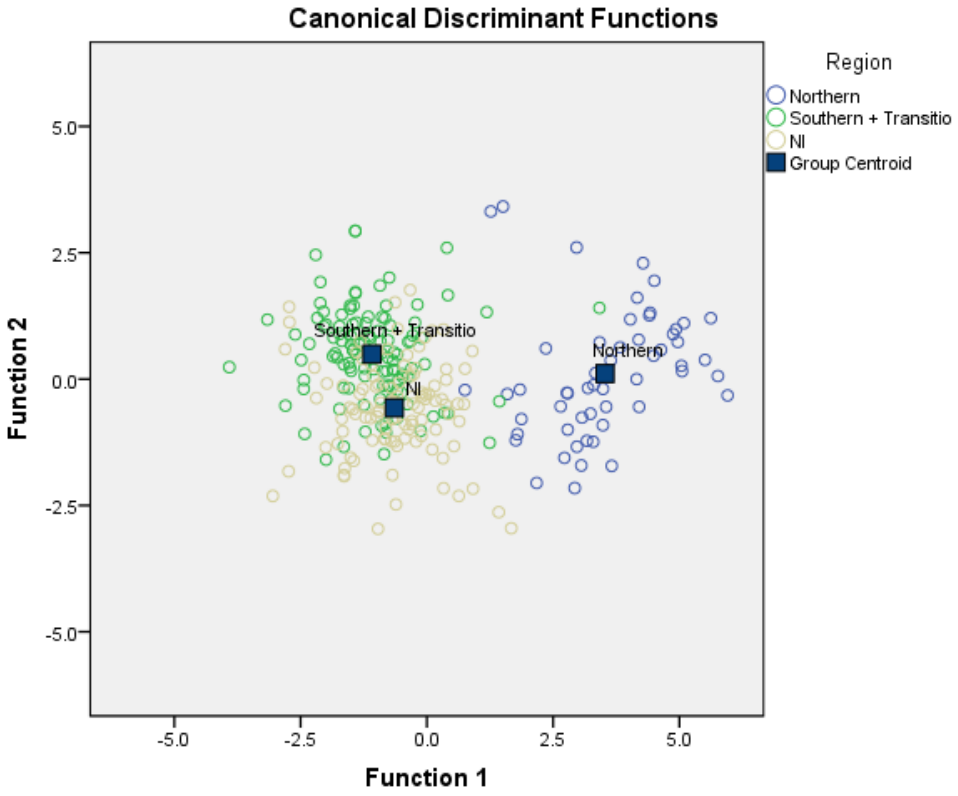


Figure 8.6 – Discriminant function plot of three sampling regions

As figure 8.6 demonstrates, there is a clear difference between the Northern Chalk province samples and the Southern and Northern Ireland samples using the first and second discriminant functions. The Southern Chalk samples are not particularly well differentiated from the Northern Ireland samples. With the groups established above, 79.1% of original cases have been correctly classified (table 8.1). The Transitional Chalk province samples are very poorly differentiated from the Southern Chalk samples, and are therefore considered here as one group (Southern + Transitional).

Table 8.1 demonstrates that the Northern province samples were classified with the highest accuracy, 96.3%, whereas the samples in the Southern + Transitional group had the lowest accuracy, at 72.3%. Samples from the NI and Southern + Transitional groups are more frequently misclassified, with over a quarter (26.8%) of Southern + Transitional samples predicted as part of the NI group.

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Northern	All NI	Southern + Transitional	
Original	Count	Northern	52	1	1	54
		All NI	0	83	24	107
		Southern + Transitional	1	30	81	112
	%	Northern	96.3	1.9	1.9	100.0
		All NI	.0	77.6	22.4	100.0
		Southern + Transitional	.9	26.8	72.3	100.0
a. 79.1% of original grouped cases correctly classified.						

Table 8.1 – SPSS classification results for Northern, Southern + Transitional, and NI groups

Within the Northern province there are three sampling locations: Yorkshire Wolds, Lincolnshire Wolds, and Yorkshire chalk. Two discriminant functions were produced, the first accounts for 98.5% of the variation, with a correspondingly high Eigenvalue (37.899) indicating the strength of its ability to discriminate between the three sampling areas. Both discriminant functions have Wilk's lambda scores that indicate that there are differences between the means of the sampling locations, however only the first discriminant function has a statistically significant *p* value (<0.001). The elements that provide the greatest discrimination are lanthanum and vanadium.

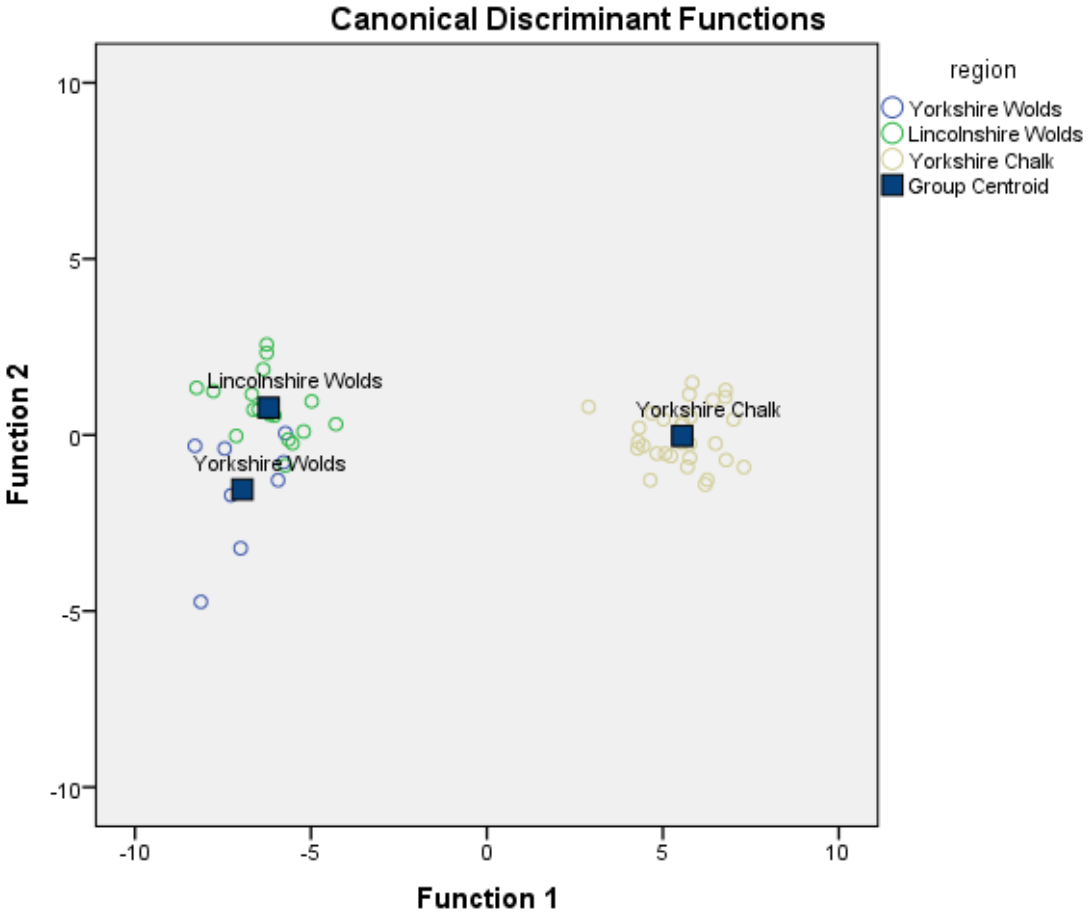


Figure 8.7 – Discriminant function plot of Northern sampling regions

Figure 8.7 demonstrates the clear separation of the Yorkshire chalk samples from the flint samples obtained from the Yorkshire and Lincolnshire Wolds, this separation is most defined along the x-axis (discriminant function 1). The samples from these three areas are correctly classified 96.3% of the time, with the only misclassification occurring between the Wolds sampling areas (table 8.2).

Classification Results[a]						
		region	Predicted Group Membership			Total
			Yorkshire Wolds	Lincolnshire Wolds	Yorkshire Chalk	
Original	Count	Yorkshire Wolds	7	1	0	8
		Lincolnshire Wolds	1	16	0	17
		Yorkshire Chalk	0	0	29	29
	%	Yorkshire Wolds	87.5	12.5	.0	100.0
		Lincolnshire Wolds	5.9	94.1	.0	100.0
		Yorkshire Chalk	.0	.0	100.0	100.0
a. 96.3% of original grouped cases correctly classified.						

Table 8.2 – SPSS classification results for Northern sampling locations

The Southern + Transitional group contains four sampling areas: Transitional, North/South Downs, Salisbury Plain/Pewsey, and Southwestern chalk. Three discriminant functions were produced. All three functions are statistically significant (p=<0.05), the first function accounts for 41.3% of the variance between the groups. The overall classification accuracy is lower than that for the Northern province; 67.9% of samples from the Southern + Transitional group were correctly classified (table 8.3).

Classification Results[a]							
		region	Predicted Group Membership				Total
			Trans Province	N/S Downs	S Plain/Pewsey	SW Chalk	
Original	Count	Trans. Prov.	16	1	0	0	17
		N/S Downs	8	34	7	9	58
		S Plain/Pewsey	2	1	14	3	20
		SW Chalk	1	3	1	12	17
	%	Trans. Province	94.1	5.9	.0	.0	100.0
		N/S Downs	13.8	58.6	12.1	15.5	100.0
		S Plain/Pewsey	10.0	5.0	70.0	15.0	100.0
		SW Chalk	5.9	17.6	5.9	70.6	100.0
a. 67.9% of original grouped cases correctly classified.							

Table 8.3 – SPSS classification results for Southern + Transitional sampling locations

The lower classification accuracy achieved with these samples is clear as there is frequent misclassification between different areas. The North/South Downs samples are misclassified the most often, with over 40% classified to the other sampling locations. These results indicate that the flint samples from the Southern + Transitional sampling locations may be potentially more difficult to accurately provenance. The elements that were most useful in distinguishing between the groups for each of the discriminant functions were: rubidium and titanium (first function), phosphorus and cerium (second function), and phosphorus and titanium (third function).

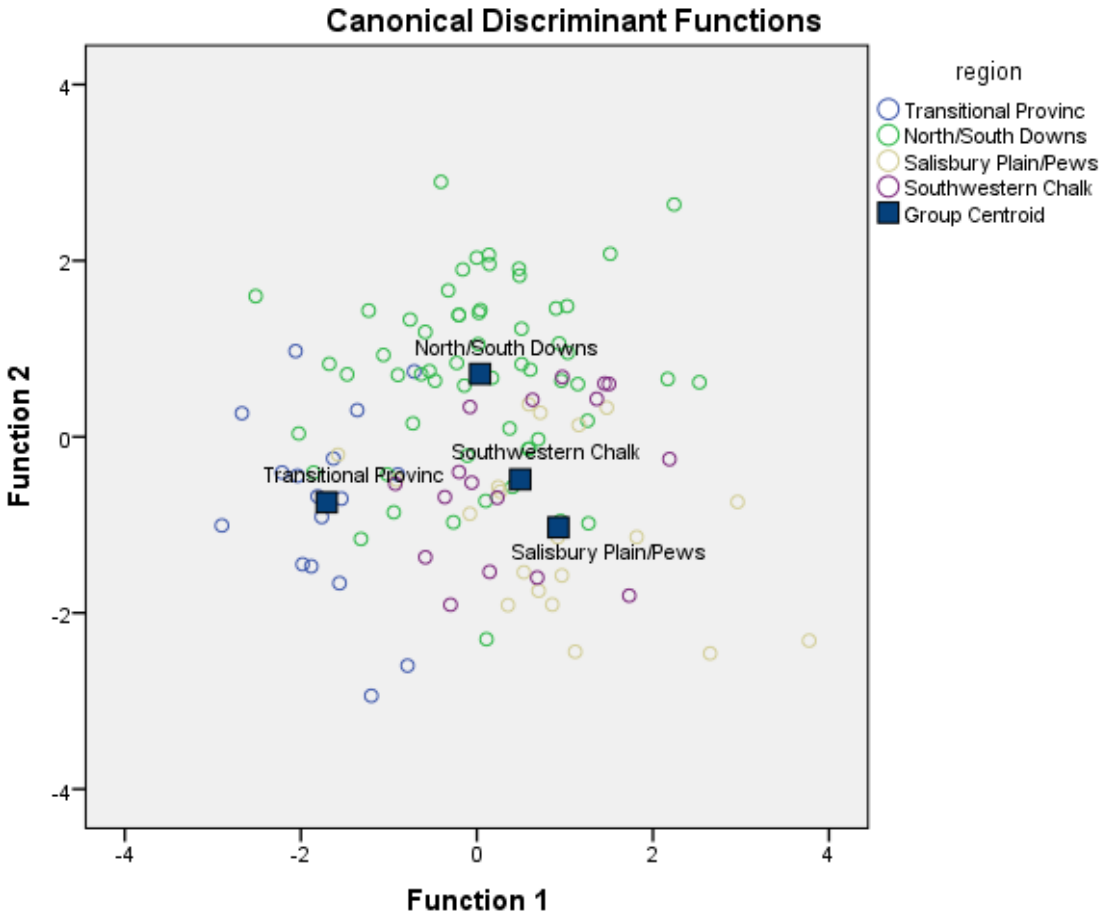


Figure 8.8 – Discriminant function plot of Southern + Transitional sampling regions

Figure 8.8 demonstrates the wide spread of results from the different sampling locations within the Southern + Transitional group, as well as the degree of overlap between each of the groups.

There were two sampling locations within the Northern Ireland group: inland and coastal. As there were only two locations, one discriminant function was produced to discriminate between them. Although the discriminant function is not interpreted as statistically significant (p=0.108), the classification results indicate that samples from the Northern Ireland sampling locations are correctly classified 81.3% of the time (table 8.4).

		region	Predicted Group Membership		Total
			Inland NI	Coastal NI	
Original	Count	Inland NI	16	1	17
		Coastal NI	19	71	90
	%	Inland NI	94.1	5.9	100.0
		Coastal NI	21.1	78.9	100.0
a. 81.3% of original grouped cases correctly classified.					

Table 8.4 – SPSS classification results for Northern Ireland sampling locations

Phosphorus and iron were the most elements in distinguishing between samples from inland and coastal locations.

8.2.1 Kintyre artefacts

Analysis of the 51 Kintyre artefacts shows broad affiliation to the group of Northern province samples (figure 8.9).

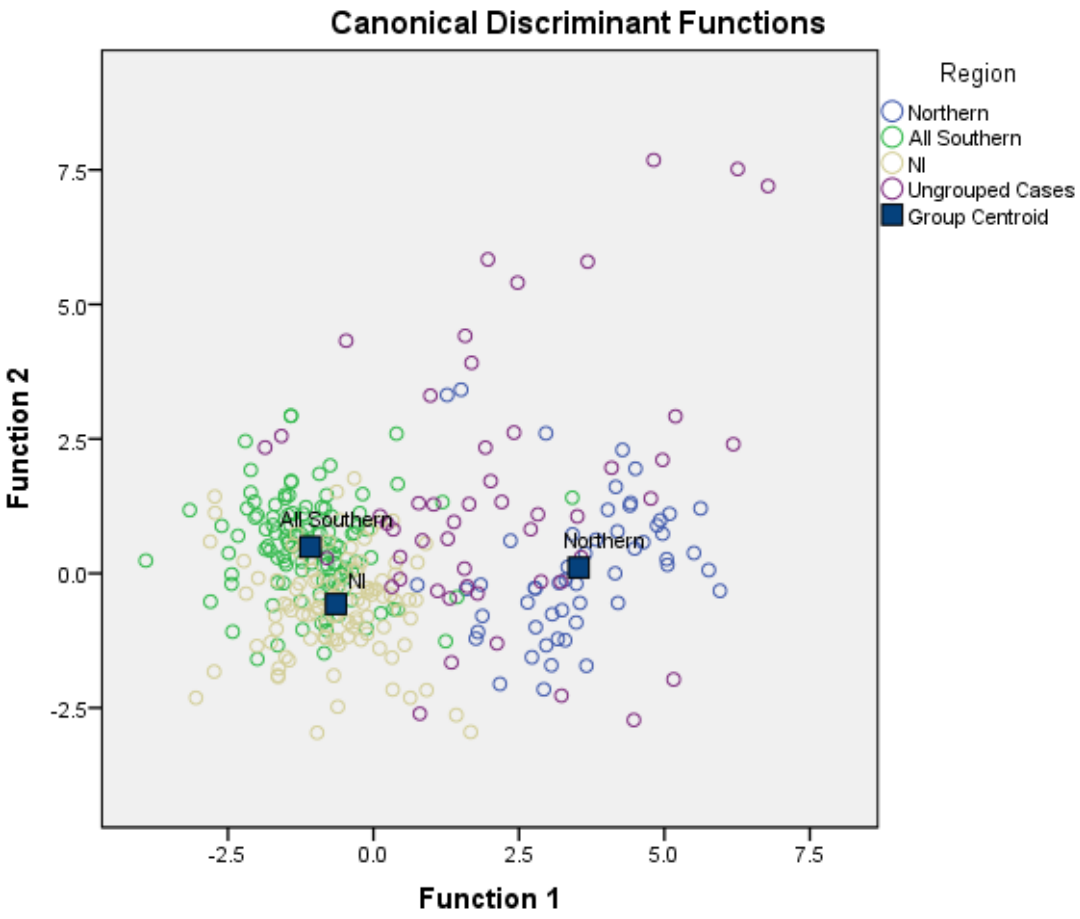


Figure 8.9 – Discriminant function plot of three sampling regions and Kintyre artefacts ('ungrouped cases')

This is supported by the classification results (table 8.5) which show that the majority (32, 62.7%) of artefacts have been classified to the Northern group.

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Northern	Southern + Transitional	NI	
Original	Count	Northern	52	1	1	54
		Southern + Transitional	1	81	30	112
		NI	0	24	83	107
		Ungrouped cases	32	10	9	51
	%	Northern	96.3	1.9	1.9	100.0
		Southern + Transitional	.9	72.3	26.8	100.0
		NI	.0	22.4	77.6	100.0
		Ungrouped cases	62.7	19.6	17.6	100.0
a. 79.1% of original grouped cases correctly classified.						

Table 8.5 - SPSS classification results: predicted membership of Kintyre artefacts

The remainder of the Kintyre artefacts are almost evenly split between the Southern + Transitional and NI groups. As stated above, the Southern + Transitional and NI samples are more frequently misclassified than either of these regions are with the Northern group.

Looking in detail at the artefacts placed within the Northern group, the majority group with the samples from Chalk flint (figure 8.10).

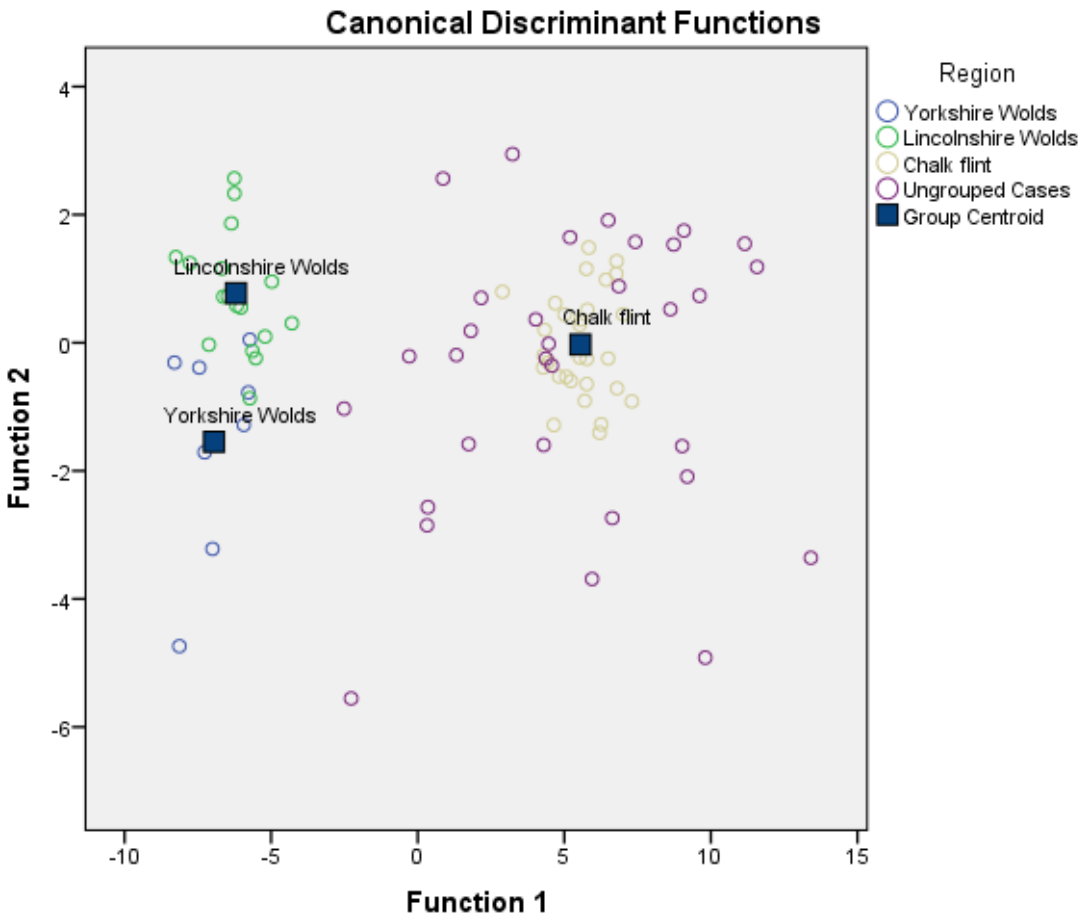


Figure 8.10 – Discriminant function plot of Northern province sampling locations and 30 Kintyre artefacts ('ungrouped cases')

The classification results show that the majority of artefacts from Kintyre (30) assigned to the Northern group are further classified into the Chalk flint group of samples (table 8.6). One artefact has been assigned to each of the Wolds groups.

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Yorkshire Wolds	Lincolnshire Wolds	Chalk flint	
Original	Count	Yorkshire Wolds	7	1	0	8
		Lincolnshire Wolds	1	16	0	17
		Chalk flint	0	0	29	29
		Ungrouped cases	1	1	30	32
	%	Yorkshire Wolds	87.5	12.5	.0	100.0
		Lincolnshire Wolds	5.9	94.1	.0	100.0
		Chalk flint	.0	.0	100.0	100.0
		Ungrouped cases	3.1	3.1	93.8	100.0
a. 96.3% of original grouped cases correctly classified.						

Table 8.6 - SPSS classification results: predicted membership of Kintyre artefacts within Northern Chalk province

Ten artefacts were allocated to the Southern + Transitional group (table 8.7). When plotted, they are loosely grouped around the samples from the southwest of England – Salisbury Plain/Pewsey and Southwestern Chalk groups.

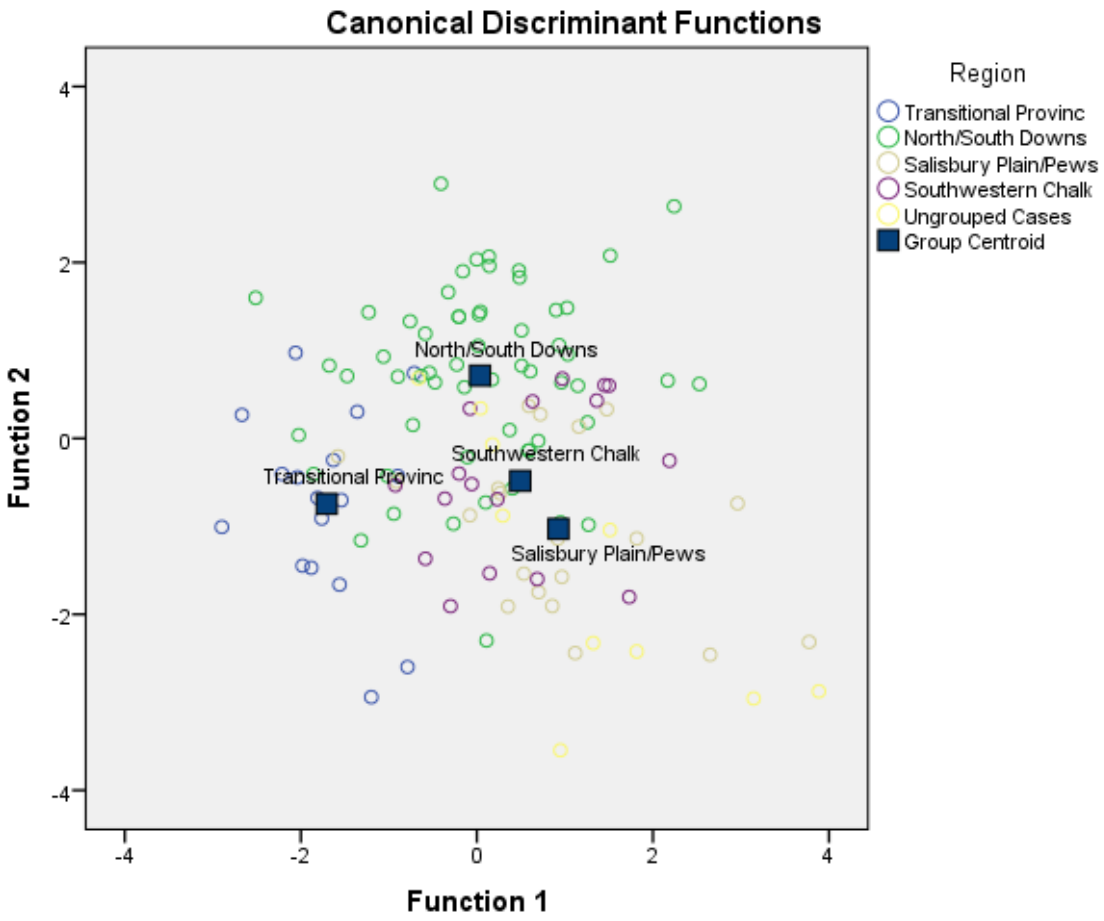


Figure 8.11 – Discriminant function plot of Southern province sampling locations and ten Kintyre artefacts ('ungrouped cases')

The classification table (table 8.7) confirms that the Kintyre artefacts classified to the Southern + Transitional group are split between the Salisbury Plain/Pewsey and Southwestern Chalk groups. Both of these groups have high classification accuracies (70% and 70.6% respectively); however there is the potential for misclassification with other groups in the Southern Chalk province.

Classification Results[a]							
		Region	Predicted Group Membership				Total
			Trans. Prov.	N/S Downs	S.Plain/ Pewsey	SW Chalk	
Original	Count	Trans. Prov.	16	1	0	0	17
		N/S Downs	8	34	7	9	58
		S. Plain/Pewsey	2	1	14	3	20
		SW Chalk	1	3	1	12	17
		Ungrouped cases	0	0	4	6	10
	%	Trans. Prov.	94.1	5.9	.0	.0	100.0
		N/S Downs	13.8	58.6	12.1	15.5	100.0
		S. Plain/Pewsey	10.0	5.0	70.0	15.0	100.0
		SW Chalk	5.9	17.6	5.9	70.6	100.0
		Ungrouped cases	.0	.0	40.0	60.0	100.0
a. 67.9% of original grouped cases correctly classified.							

Table 8.7 - SPSS classification results: predicted membership of 10 Kintyre artefacts within Southern Chalk province

Nine Kintyre artefacts were assigned to the NI sample group. The majority of these (6, 66.7%) group with flint samples collected from coastal locations, however 21.1% of coastal samples are misclassified as belonging to the inland group (table 8.8).

Classification Results[a]					
		Region	Predicted Group Membership		Total
			Inland	Coastal	
Original	Count	Inland	16	1	17
		Coastal	19	71	90
		Ungrouped cases	3	6	9
	%	Inland	94.1	5.9	100.0
		Coastal	21.1	78.9	100.0
		Ungrouped cases	33.3	66.7	100.0
a. 81.3% of original grouped cases correctly classified.					

Table 8.8 - SPSS classification results: predicted membership of 9 Kintyre artefacts within Northern Ireland Chalk formation

It was anticipated that the samples from Kintyre would be potentially difficult to provenance as the main source of raw material would likely have been beach pebbles, which may have been eroded from a number of potential chalk outcrops. This, coupled with the wide temporal span of the artefacts, may result in a large variety of potential source regions. This is reflected in the results above, as samples have been provenanced to sources in the north of Ireland, southwestern England, as well as Wolds and Chalk flint in the north of England.

The chalk in the north of Ireland originally extended northeast into Scotland and although it has since been mostly weathered away, beach pebbles along the western coast of Scotland are likely to have ultimately originated from this chalk (Harding *et. al.* 2004, 81). The geochemical similarity of the flint from the north of Ireland and south of England may lead to confusion with samples from Kintyre, as beach pebbles on Kintyre that have eroded from chalk in the

north of Ireland may appear very similar to flint from the south of England. This may lead to samples being incorrectly provenanced to the Southern or Transitional Chalk provinces.

8.2.2 Threefords artefacts

Of the 20 artefacts in the Threefords assemblage, twelve are made from a dark grey flint; the remaining eight are either buff-coloured (two), light grey (five), or orange/brown (one).

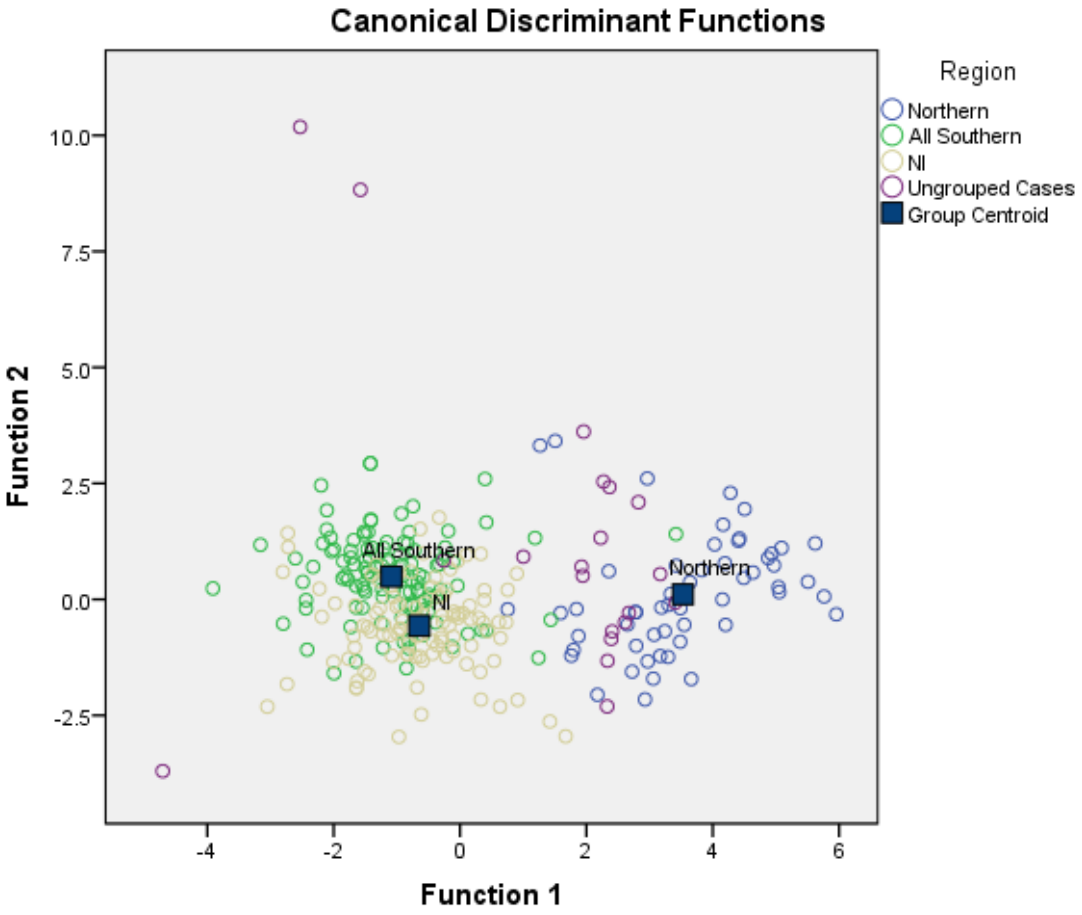


Figure 8.12 – Discriminant function plot of three sampling locations and Threefords artefacts ('ungrouped cases')

Plotted, the Threefords artefacts group most closely with the Northern flint samples (figure 8.12). The classification results indicate that a small number of the Threefords artefacts are classified as belonging to the Southern + Transitional (four) and NI (one) groups (table 8.9).

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Northern	Southern + Transitional	NI	
Original	Count	Northern	52	1	1	54
		Southern + Transitional	1	81	30	112
		NI	0	24	83	107
		Ungrouped cases	15	4	1	20
	%	Northern	96.3	1.9	1.9	100.0
		Southern + Transitional	.9	72.3	26.8	100.0
		NI	.0	22.4	77.6	100.0
		Ungrouped cases	75.0	20.0	5.0	100.0
a. 79.1% of original grouped cases correctly classified.						

Table 8.9 - SPSS classification results: predicted membership of 20 Threefords artefacts within Northern Ireland Chalk formation

The majority of artefacts from Threefords (15, 96.3%) are classified to the Northern group. When compared to the sampling locations within the Northern province (figure 8.13), all but one of these Threefords artefacts are classified into the Chalk flint group (table 8.10). The remaining artefact is classified to the Yorkshire Wolds (table 8.10).

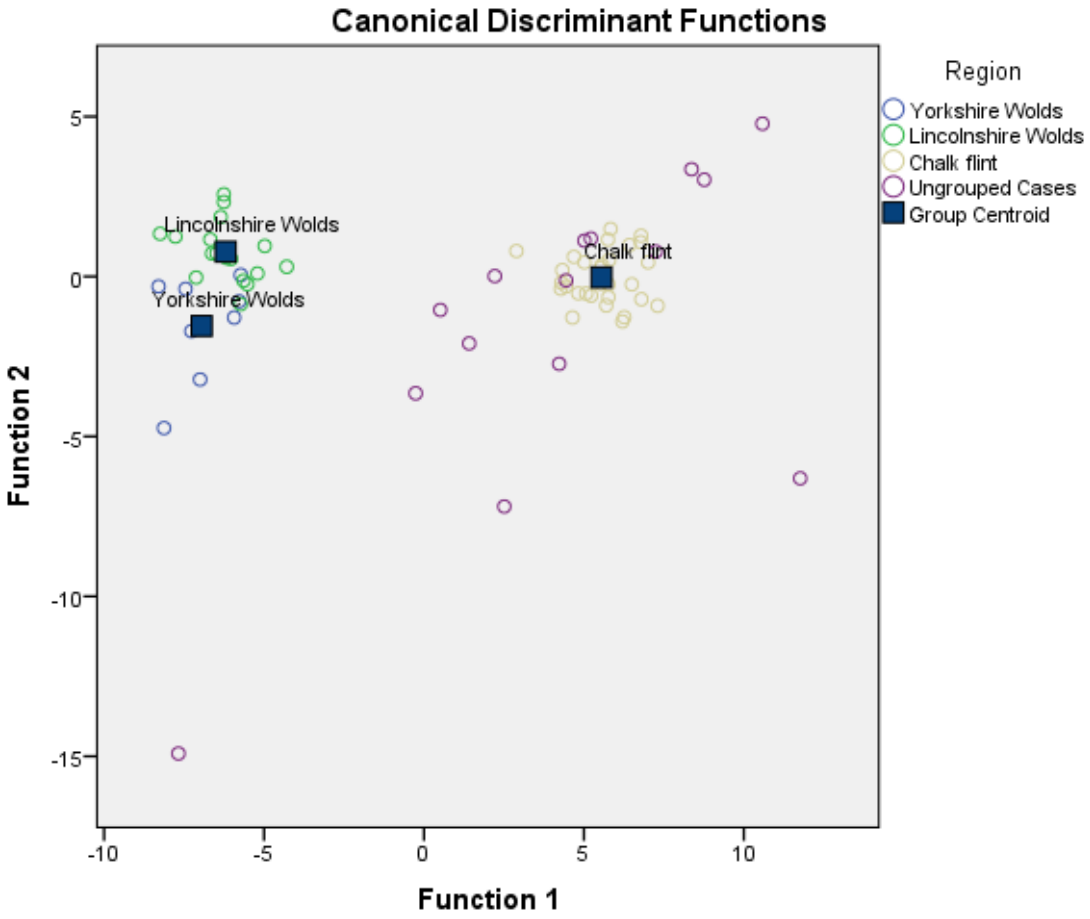


Figure 8.13 – Discriminant function plot of Northern sampling locations and 15 Threefords artefacts ('ungrouped cases')

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Yorkshire Wolds	Lincolnshire Wolds	Chalk flint	
Original	Count	Yorkshire Wolds	7	1	0	8
		Lincolnshire Wolds	1	16	0	17
		Chalk flint	0	0	29	29
		Ungrouped cases	1	0	14	15
	%	Yorkshire Wolds	87.5	12.5	.0	100.0
		Lincolnshire Wolds	5.9	94.1	.0	100.0
		Chalk flint	.0	.0	100.0	100.0
		Ungrouped cases	6.7	.0	93.3	100.0
a. 96.3% of original grouped cases correctly classified.						

Table 8.10 - SPSS classification results: predicted membership of 15 Threefords artefacts within Northern Chalk province

Four artefacts from Threefords were classified to the Southern + Transitional group (table 8.11). When compared to the sampling locations, three artefacts grouped with the Salisbury Plain/Pewsey flint samples; the remaining artefact to the North/South Downs (table 8.11).

Classification Results[a]							
		Region	Predicted Group Membership				Total
			Trans. Prov.	N/S Downs	S.Plain/ Pewsey	SW Chalk	
Original	Count	Trans.Prov.	16	1	0	0	17
		N/S Downs	8	34	7	9	58
		S. Plain/Pewsey	2	1	14	3	20
		SW Chalk	1	3	1	12	17
		Ungrouped cases	0	1	3	0	4
	%	Trans.Prov.	94.1	5.9	.0	.0	100.0
		N/S Downs	13.8	58.6	12.1	15.5	100.0
		S. Plain/Pewsey	10.0	5.0	70.0	15.0	100.0
		SW Chalk	5.9	17.6	5.9	70.6	100.0
		Ungrouped cases	.0	25.0	75.0	.0	100.0
a. 67.9% of original grouped cases correctly classified.							

Table 8.11 - SPSS classification results: predicted membership of 4 Threefords artefacts within Southern Chalk province

One artefact from Threefords was grouped with the samples from Northern Ireland. When analysed with comparison to the samples from this area, it appears to match most closely with the samples obtained from the inland source in the north of Ireland (table 8.12).

Classification Results[a]					
		Region	Predicted Group Membership		Total
			Inland	Coastal	
Original	Count	Inland	16	1	17
		Coastal	19	71	90
		Ungrouped cases	1	0	1
	%	Inland	94.1	5.9	100.0
		Coastal	21.1	78.9	100.0
		Ungrouped cases	100.0	.0	100.0
a. 81.3% of original grouped cases correctly classified.					

Table 8.12 - SPSS classification results: predicted membership of 1 Threefords artefact within Northern Ireland Chalk formation

Samples from the coastal locations are frequently misclassified as inland (21.1% misclassified) (table 8.12), meaning that the artefact from Threefords may in fact be from a coastal source.

8.2.3 Nether Exe enclosure artefacts

The discriminant function plot illustrates the grouping of the Nether Exe artefacts (figure 8.14) compared to flint samples from three different Chalk provinces.

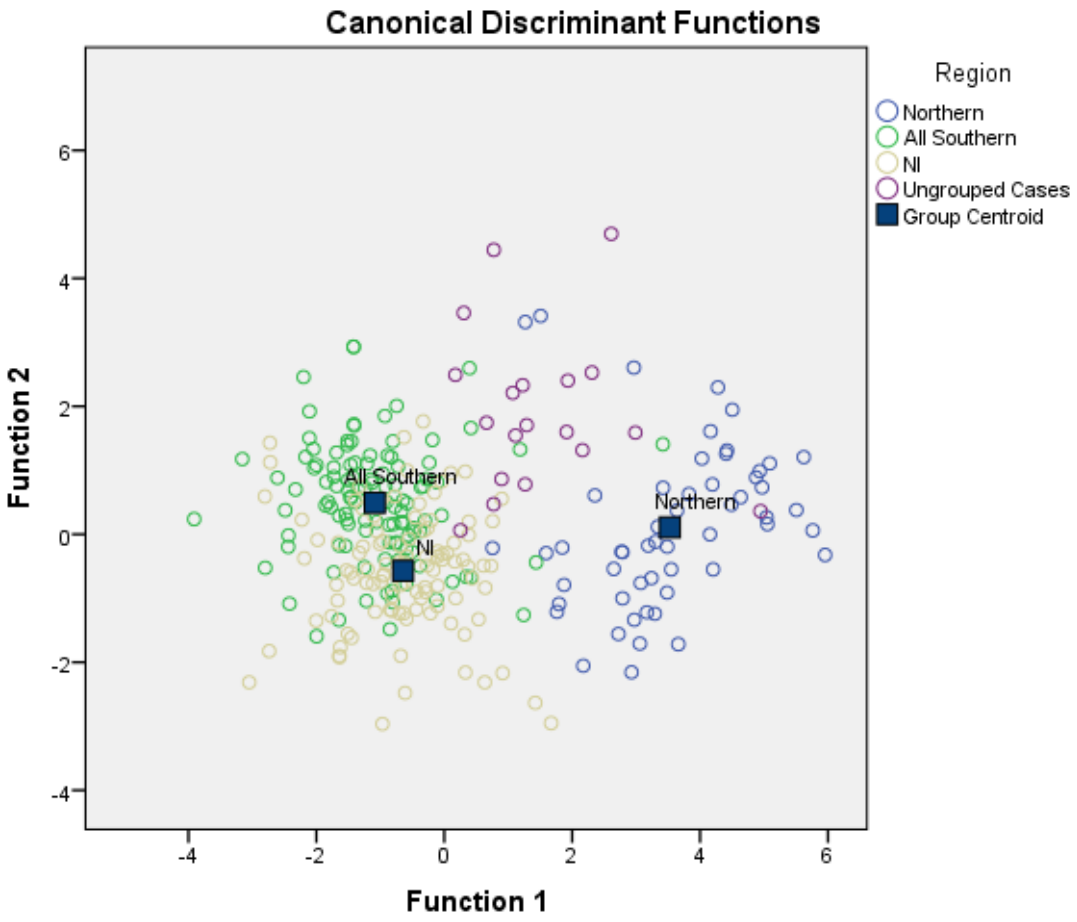


Figure 8.14 – Discriminant function plot of three sampling locations and Nether Exe artefacts ('ungrouped cases')

The classification results below show that the majority (9, 45%) of Nether Exe artefacts are classified to the Southern + Transitional group. Three artefacts are classified to the Northern Ireland group, however over a quarter (26.6%) of Southern + Transitional samples are misclassified as belonging to the NI group, raising the possibility that the Nether Exe samples classified to NI may belong in the Southern + Transitional group. Almost half of the nether Exe artefacts were classified to the Northern group (8, 40%).

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Northern	Southern + Transitional	NI	
Original	Count	Northern	52	1	1	54
		Southern + Transitional	1	81	30	112
		NI	0	24	83	107
		Ungrouped cases	8	9	3	20
	%	Northern	96.3	1.9	1.9	100.0
		Southern + Transitional	.9	72.3	26.8	100.0
		NI	.0	22.4	77.6	100.0
		Ungrouped cases	40.0	45.0	15.0	100.0
a. 79.1% of original grouped cases correctly classified.						

Table 8.13 - SPSS classification results: predicted membership of Nether Exe artefacts

The Nether Exe samples that are assigned Southern + Transitional group membership are plotted against sampling locations in figure 8.15.

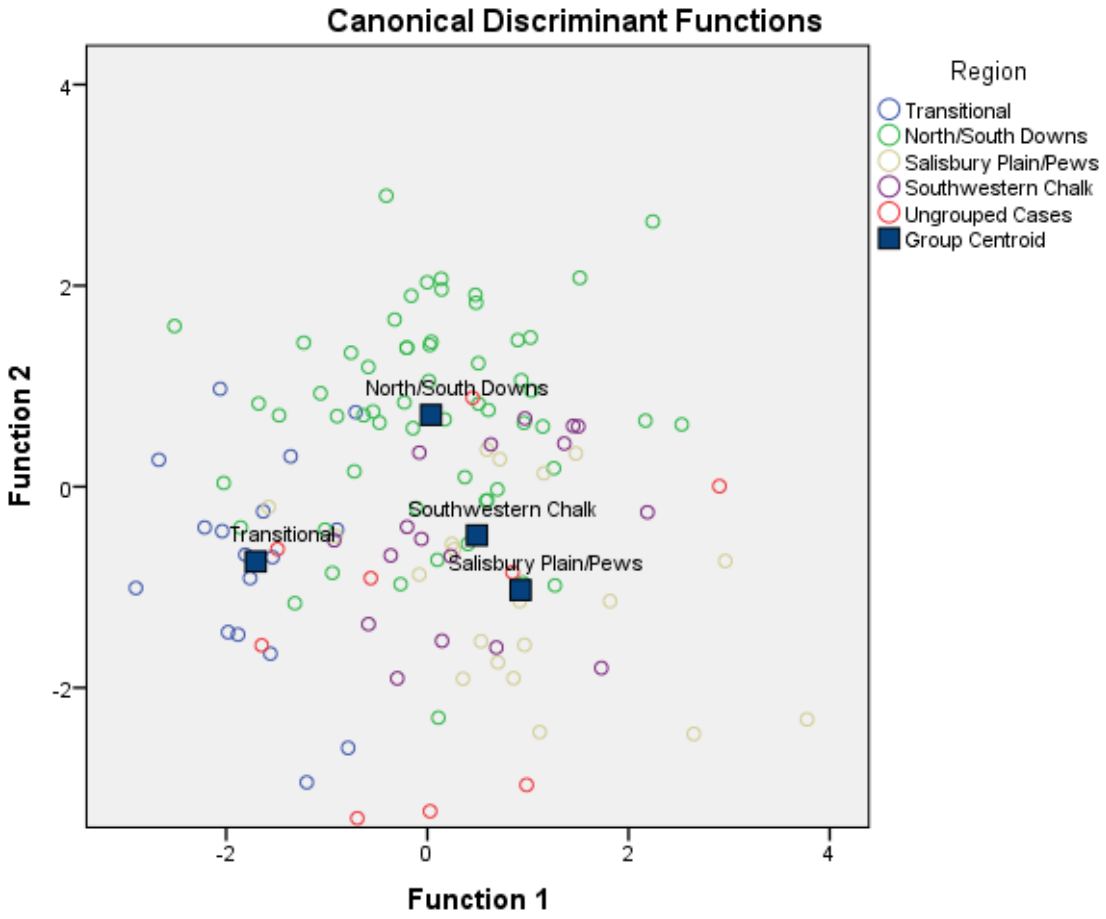


Figure 8.15 – Discriminant function plot of Southern and Transitional sampling locations and 9 Nether Exe artefacts ('ungrouped cases')

The Nether Exe samples are widely distributed throughout the Transitional and Southern sampling locations, and are variously classified into all four sampling regions within the Southern + Transitional group (table 8.14).

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Trans. Prov.	N/S Downs	S.Plain/ Pewsey	SW Chalk	
Original	Count	Trans.Prov.	16	1	0	0	17
		N/S Downs	8	34	7	9	58
		S. Plain/Pewsey	2	1	14	3	20
		SW Chalk	1	3	1	12	17
		Ungrouped cases	2	1	3	3	9
	%	Trans.Prov.	94.1	5.9	.0	.0	100.0
		N/S Downs	13.8	58.6	12.1	15.5	100.0
		S. Plain/Pewsey	10.0	5.0	70.0	15.0	100.0
		SW Chalk	5.9	17.6	5.9	70.6	100.0
		Ungrouped cases	22.2	11.1	33.3	33.3	100.0
a. 67.9% of original grouped cases correctly classified.							

Table 8.14 - SPSS classification results: predicted membership of 9 Nether Exe artefacts within Southern + Transitional group

The majority of the artefacts classified to the Southern + Transitional group came from the southwest of England; three artefacts are allocated to the Salisbury Plain/Pewsey and three to the Southwestern chalk sampling locations.

Eight of the Nether Exe artefacts grouped with the Northern samples (table 8.15). Compared to the sampling locations in the Northern Chalk province, six (75%) are allocated to the Chalk flint group, the remainder to the Yorkshire Wolds (table 8.15).

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Yorkshire Wolds	Lincolnshire Wolds	Chalk flint	
Original	Count	Yorkshire Wolds	7	1	0	8
		Lincolnshire Wolds	1	16	0	17
		Chalk flint	0	0	29	29
		Ungrouped cases	2	0	6	8
	%	Yorkshire Wolds	87.5	12.5	.0	100.0
		Lincolnshire Wolds	5.9	94.1	.0	100.0
		Chalk flint	.0	.0	100.0	100.0
		Ungrouped cases	25.0	.0	75.0	100.0
a. 96.3% of original grouped cases correctly classified.						

Table 8.15 - SPSS classification results: predicted membership of 8 Nether Exe artefacts within 'Northern' group

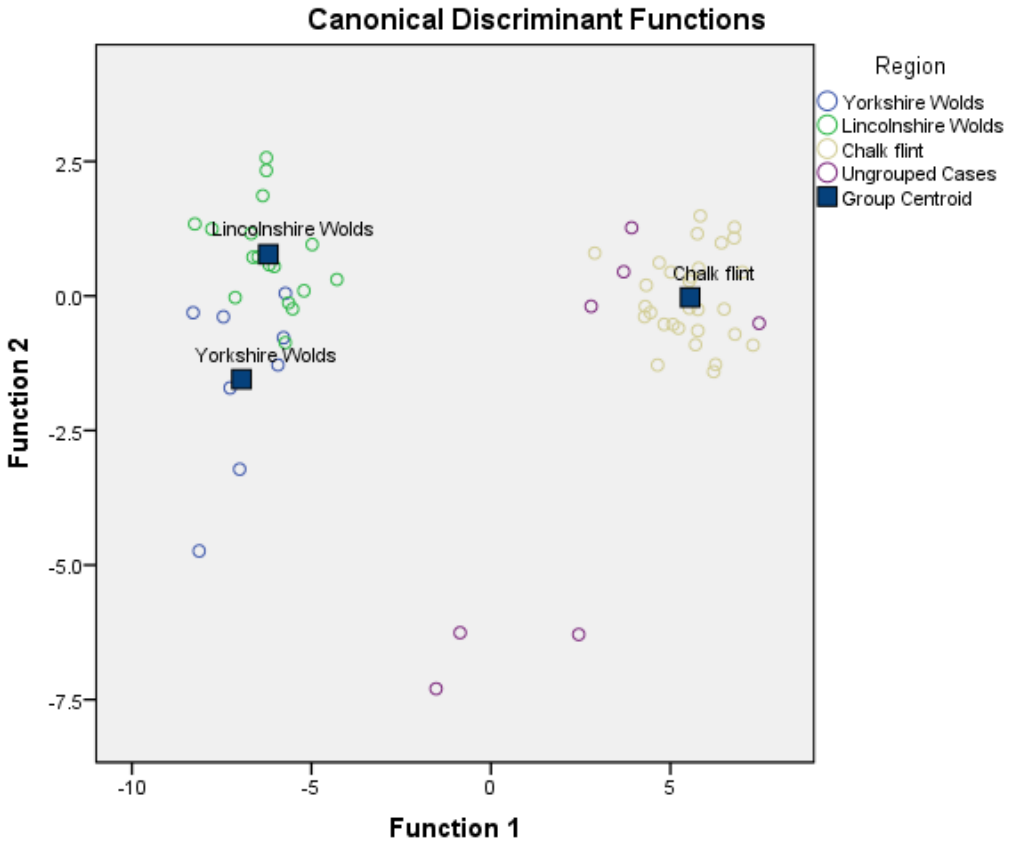


Figure 8.16 – Discriminant function plot of Northern sampling locations and 8 Nether Exe artefacts ('ungrouped cases')

Three Nether Exe artefacts are classified to the Northern Ireland group; two are grouped with the coastal flint samples, and one with inland flint samples (table 8.16).

Classification Results[a]					
		Region	Predicted Group Membership		Total
			Inland	Coastal	
Original	Count	Inland	16	1	17
		Coastal	19	71	90
		Ungrouped cases	1	2	3
	%	Inland	94.1	5.9	100.0
		Coastal	21.1	78.9	100.0
		Ungrouped cases	33.3	66.7	100.0
a. 81.3% of original grouped cases correctly classified.					

Table 8.16 - SPSS classification results: predicted membership of 3 Nether Exe artefacts within Northern Ireland group

Coastal sources are frequently misclassified as inland (21.1% of the time), potentially the Nether Exe artefact classified as inland may actually be from one of the coastal locations.

8.2.4 N1F recollection artefacts

The N1F recollection artefacts are plotted against the three main sampling regions in figure 8.17.

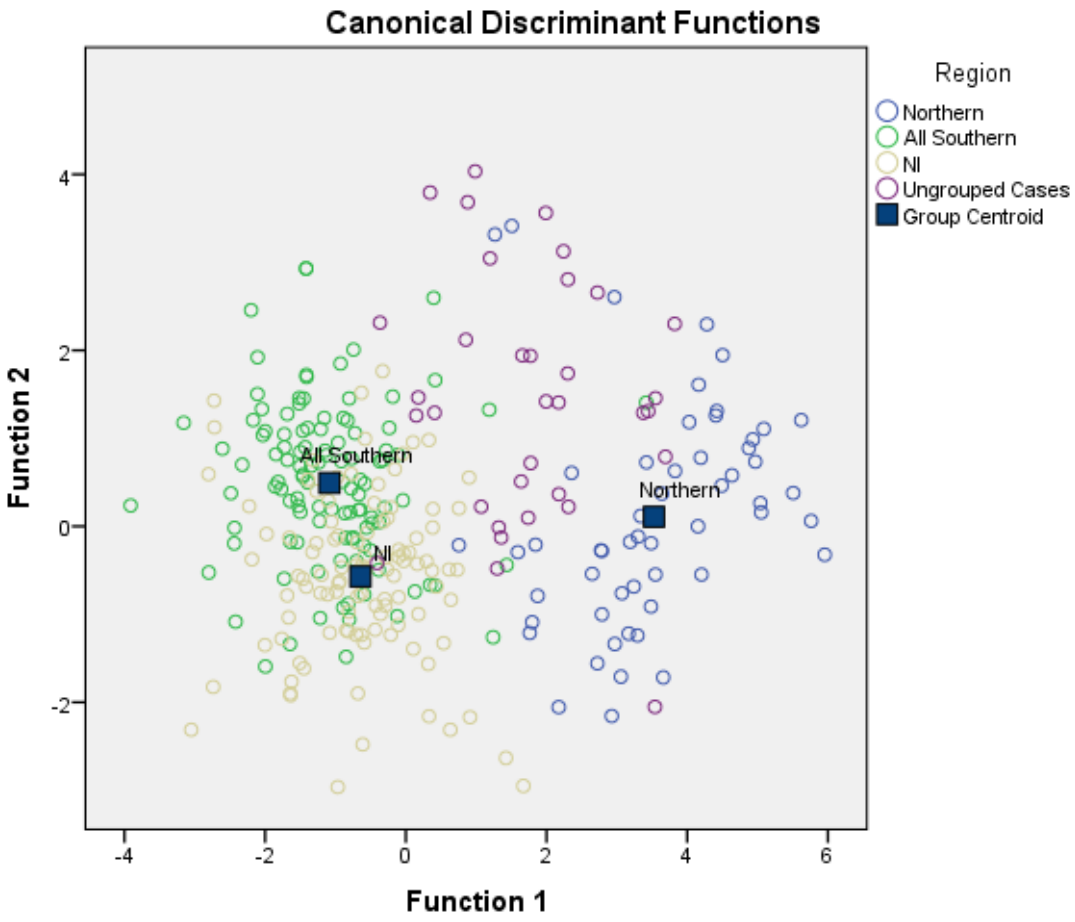


Figure 8.17 – Discriminant function plot of three sampling locations and 34 N1F recollection artefacts ('ungrouped cases')

The N1F artefacts are broadly distributed, but the classification results indicate that they are mostly (20, 58.8%) grouped with the Northern flint samples (table 8.17).

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Northern	Southern + Transitional	NI	
Original	Count	Northern	52	1	1	54
		Southern + Transitional	1	81	30	112
		NI	0	24	83	107
		Ungrouped cases	20	9	5	34
	%	Northern	96.3	1.9	1.9	100.0
		Southern + Transitional	.9	72.3	26.8	100.0
		NI	.0	22.4	77.6	100.0
		Ungrouped cases	58.8	26.5	14.7	100.0
a. 79.1% of original grouped cases correctly classified.						

Table 8.17 - SPSS classification results: predicted membership of N1F recollection artefacts

Five N1F artefacts are grouped with the Northern Ireland flint samples, and nine within the Southern + Transitional group. As stated above, over a quarter (26.8%) of Southern + Transitional flint samples are misclassified as belonging to NI group, and over a fifth of NI samples are misclassified as belonging to the Southern + Transitional group. Northern group flint samples are correctly classified 96.3% of the time.

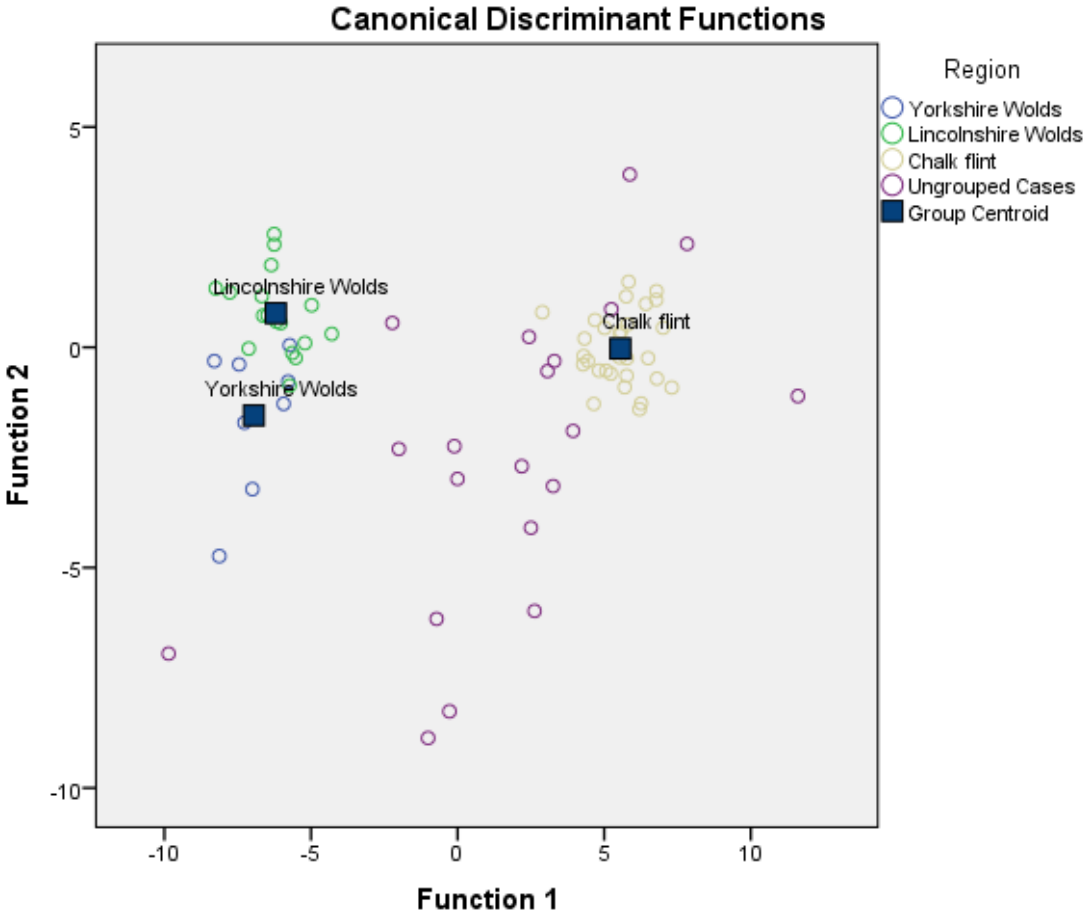


Figure 8.18 – Discriminant function plot of Northern sampling locations and 20 N1F recollection artefacts ('ungrouped cases')

Compared with the Northern Chalk province sampling regions (figure 8.18), the N1F artefacts are broadly distributed, but the majority (14, 70%) are grouped with the samples obtained from Chalk flint (table 8.18).

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Yorkshire Wolds	Lincolnshire Wolds	Chalk flint	
Original	Count	Yorkshire Wolds	7	1	0	8
		Lincolnshire Wolds	1	16	0	17
		Chalk flint	0	0	29	29
		Ungrouped cases	5	1	14	20
	%	Yorkshire Wolds	87.5	12.5	.0	100.0
		Lincolnshire Wolds	5.9	94.1	.0	100.0
		Chalk flint	.0	.0	100.0	100.0
		Ungrouped cases	25.0	5.0	70.0	100.0
a. 96.3% of original grouped cases correctly classified.						

Table 8.18 - SPSS classification results: predicted membership of 20 N1F recollection artefacts within Northern Chalk province

The remainder of the artefacts are from the Yorkshire Wolds (5, 25%), and Lincolnshire Wolds (1, 5%).

Nine of the N1F recollection artefacts were classified with the samples obtained from the Southern and Transitional Chalk provinces (Southern + Transitional group). The majority are sourced to the southwest of England: four classified to each the Salisbury Plain/Pewsey and Southwestern Chalk groups (table 8.19). The remaining artefact is classified to the North/South Downs.

Classification Results[a]							
		Region	Predicted Group Membership				Total
			Trans. Prov.	N/S Downs	S. Plain/Pewsey	SW Chalk	
Original	Count	Trans. Prov.	16	1	0	0	17
		N/S Downs	8	34	7	9	58
		S. Plain/Pewsey	2	1	14	3	20
		SW Chalk	1	3	1	12	17
		Ungrouped cases	0	1	4	4	9
	%	Trans. Prov.	94.1	5.9	.0	.0	100.0
		N/S Downs	13.8	58.6	12.1	15.5	100.0
		S. Plain/Pewsey	10.0	5.0	70.0	15.0	100.0
		SW Chalk	5.9	17.6	5.9	70.6	100.0
		Ungrouped cases	.0	11.1	44.4	44.4	100.0
a. 67.9% of original grouped cases correctly classified.							

Table 8.19 - SPSS classification results: predicted membership of 9 N1F recollection artefacts within Southern and Transitional Chalk provinces

Figure 8.19 illustrates the distribution of the nine N1F artefacts classified to the Southern + Transitional group.

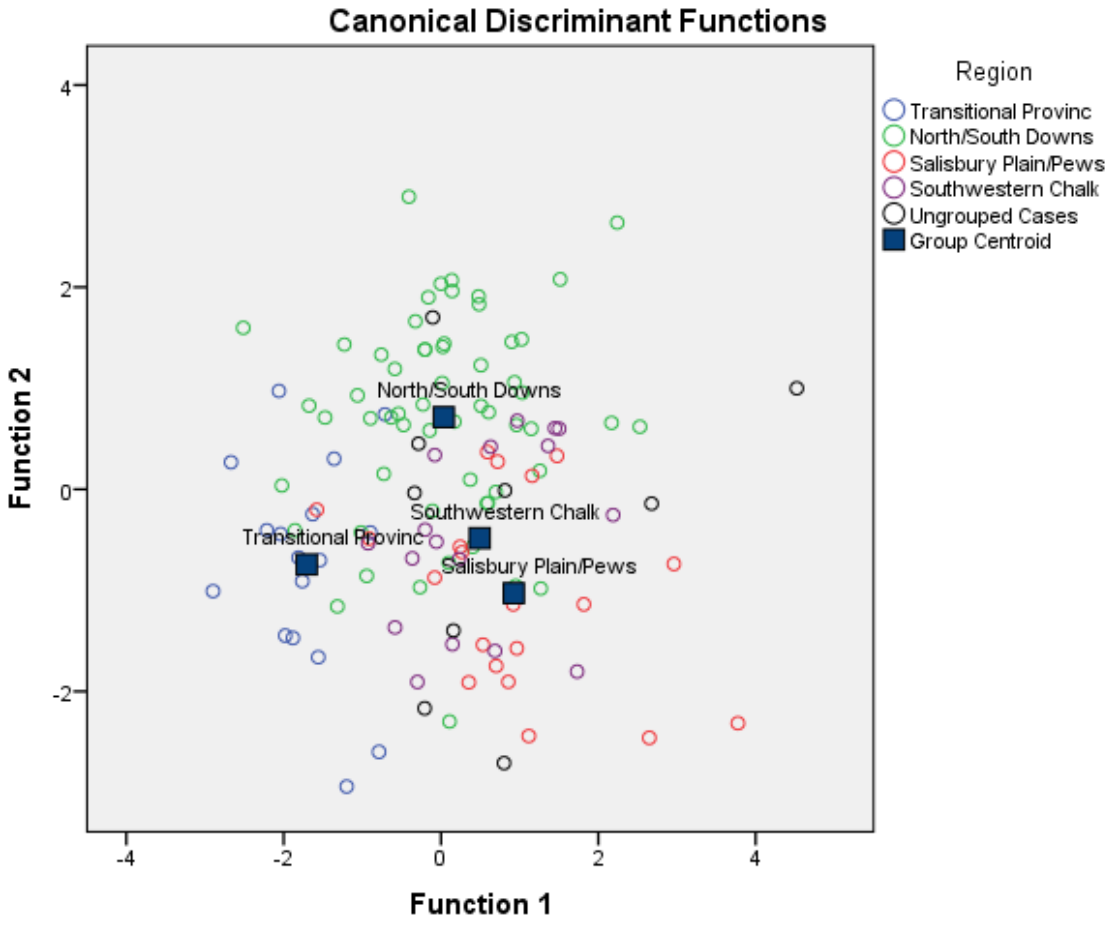


Figure 8.19 – Discriminant function plot of Southern + Transitional sampling locations and 9 N1F recollection artefacts ('ungrouped cases')

Five of the N1F recollections artefacts were classified to the Northern Ireland group (table 8.20). When these artefacts are compared to coastal and inland sampling locations, they are predominantly grouped with the coastal samples (3, 60%) (table 8.20).

Classification Results[a]					
		Region	Predicted Group Membership		Total
			Inland	Coastal	
Original	Count	Inland	16	1	17
		Coastal	19	71	90
		Ungrouped cases	2	3	5
	%	Inland	94.1	5.9	100.0
		Coastal	21.1	78.9	100.0
		Ungrouped cases	40.0	60.0	100.0
a. 81.3% of original grouped cases correctly classified.					

Table 8.20 - SPSS classification results: predicted membership of 5 N1F recollection artefacts within Northern Ireland Chalk formation

The remaining two artefacts are classified to the inland group, however there is considerable misclassification of coastal samples to the inland group (21.1%). The N1F artefacts classified to the inland group may actually be from coastal locations.

8.2.5 Bann Valley artefacts

The Bann Valley artefacts were incorporated into the discriminant function analysis as ungrouped cases and the classification results from this are shown below (table 8.21), and plotted in figure 8.20.

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Northern	All NI	Southern + Transitional	
Original	Count	Northern	52	1	1	54
		All NI	0	83	24	107
		Southern + Transitional	1	30	81	112
		Ungrouped cases	43	3	11	57
	%	Northern	96.3	1.9	1.9	100.0
		All NI	.0	77.6	22.4	100.0
		Southern + Transitional	.9	26.8	72.3	100.0
		Ungrouped cases	75.4	5.3	19.3	100.0
a. 79.1% of original grouped cases correctly classified.						

Table 8.21 – SPSS classification results: predicted membership of Bann Valley artefacts

The classification results place the majority of Bann Valley artefacts (43 artefacts, 75.4%) in the Northern group, indicating greatest similarity with flint from the north of England. Only three artefacts matched more closely with the flint samples from Northern Ireland, the remaining eleven artefacts grouped with the Southern + Transitional samples.

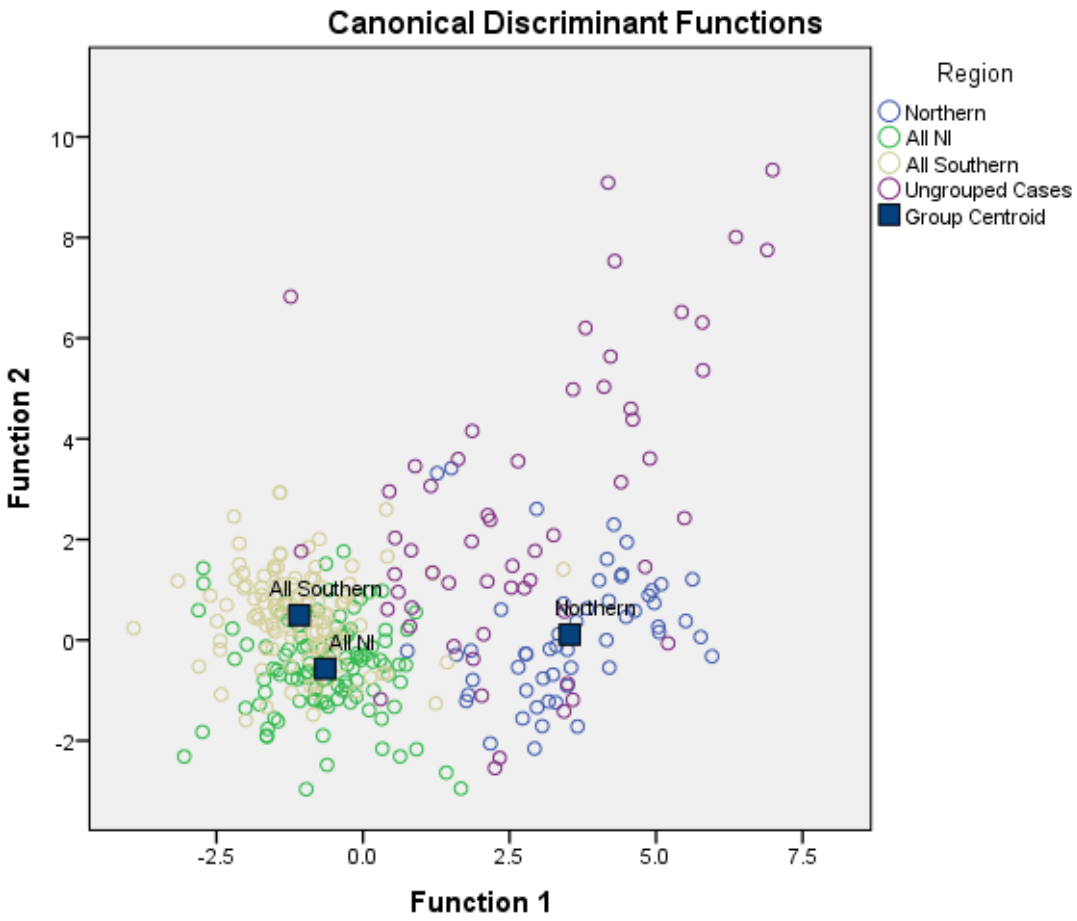


Figure 8.20 – Discriminant function plot of three sampling regions and Bann Valley artefacts ('ungrouped cases')

As the majority of artefacts (43) from the Bann Valley assemblage were classified as belonging to the Northern group, further analysis was undertaken to determine if source could be narrowed down to the three flint sources in this area: Yorkshire Wolds, Lincolnshire Wolds, or chalk flint.

The discriminant function scatterplot (figure 8.21) illustrates the broad spread of the artefacts, overlapping with the samples obtained from Yorkshire chalk flint. The classification results (table 8.22) corroborate this.

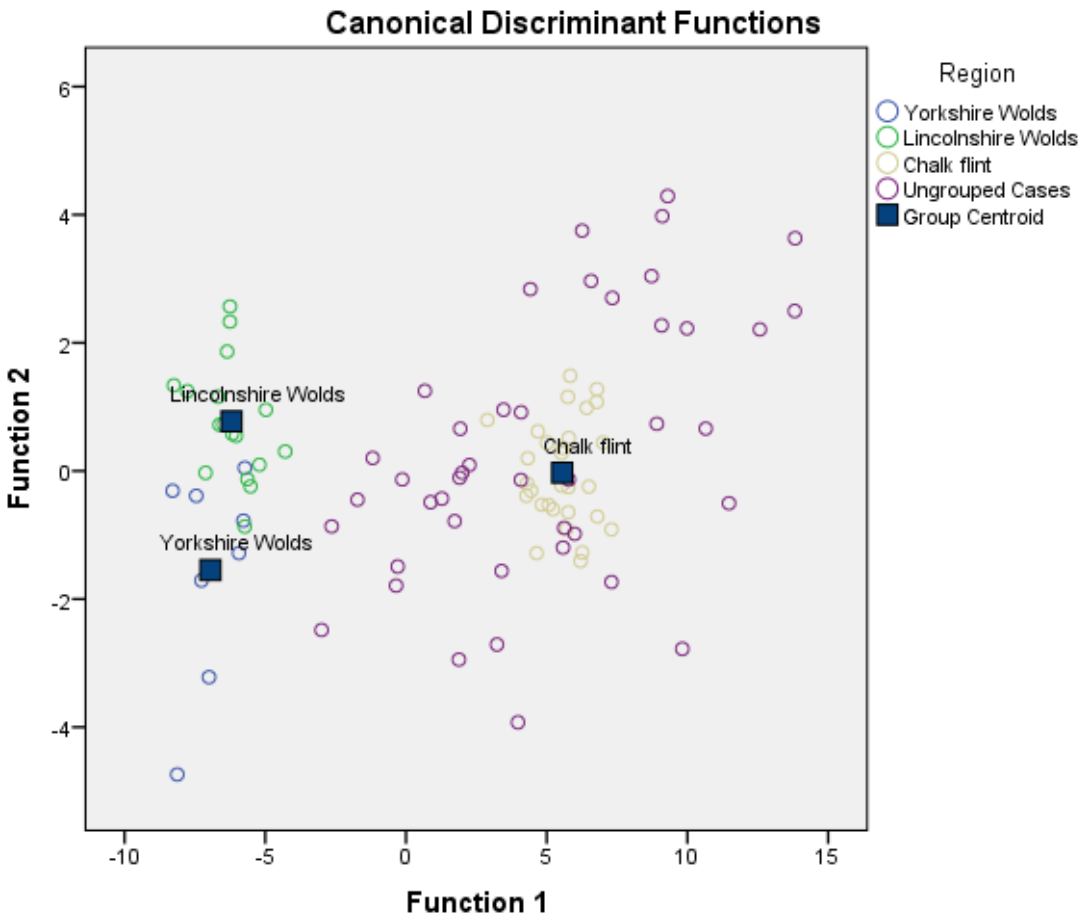


Figure 8.21 – Discriminant function plot of Northern province sampling locations and 43 Bann Valley artefacts ('ungrouped cases')

The majority of artefacts (39=90.7%) are classified as belonging to the Chalk flint group, whose sampling locations are at North Landing, East Yorkshire.

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Yorkshire Wolds	Lincolnshire Wolds	Chalk flint	
Original	Count	Yorkshire Wolds	7	1	0	8
		Lincolnshire Wolds	1	16	0	17
		Chalk flint	0	0	29	29
		Ungrouped cases	1	3	39	43
	%	Yorkshire Wolds	87.5	12.5	.0	100.0
		Lincolnshire Wolds	5.9	94.1	.0	100.0
		Chalk flint	.0	.0	100.0	100.0
		Ungrouped cases	2.3	7.0	90.7	100.0
a. 96.3% of original grouped cases correctly classified.						

Table 8.22 - SPSS classification results: predicted membership of Bann Valley artefacts within Northern Chalk province

The flint samples from within the Northern Chalk province have a high classification accuracy (96.3%). From the classification results, the Yorkshire and Lincolnshire Wolds flint samples are occasionally misclassified (one sample misclassified in each case), however they are not misclassified as belonging to the Chalk flint group (and vice versa). Taking into account that there is the potential for confusion between the Yorkshire and Lincolnshire Wolds samples, it can be stated that of the 43 Bann Valley artefacts that were classified to the Northern group (table 8.22), 39 match the samples from the Chalk flint and the remaining four are from Wolds sources.

8.2.6 Blind provenancing tests using pXRF

In total, 273 samples were analysed using pXRF. To approximate an actual assemblage, samples were randomly selected and tested as 'ungrouped cases' in the discriminant function

analysis. Samples were selected following the same procedure used for the ICP-MS samples, outlined in chapter 5.5.2. Just over 50% of the pXRF samples were selected (137 out of 273).

Using a three-group separation (Northern, Northern Ireland, and Southern + Transitional), the overall classification accuracy using discriminant function analysis is 79.1% (table 8.1).

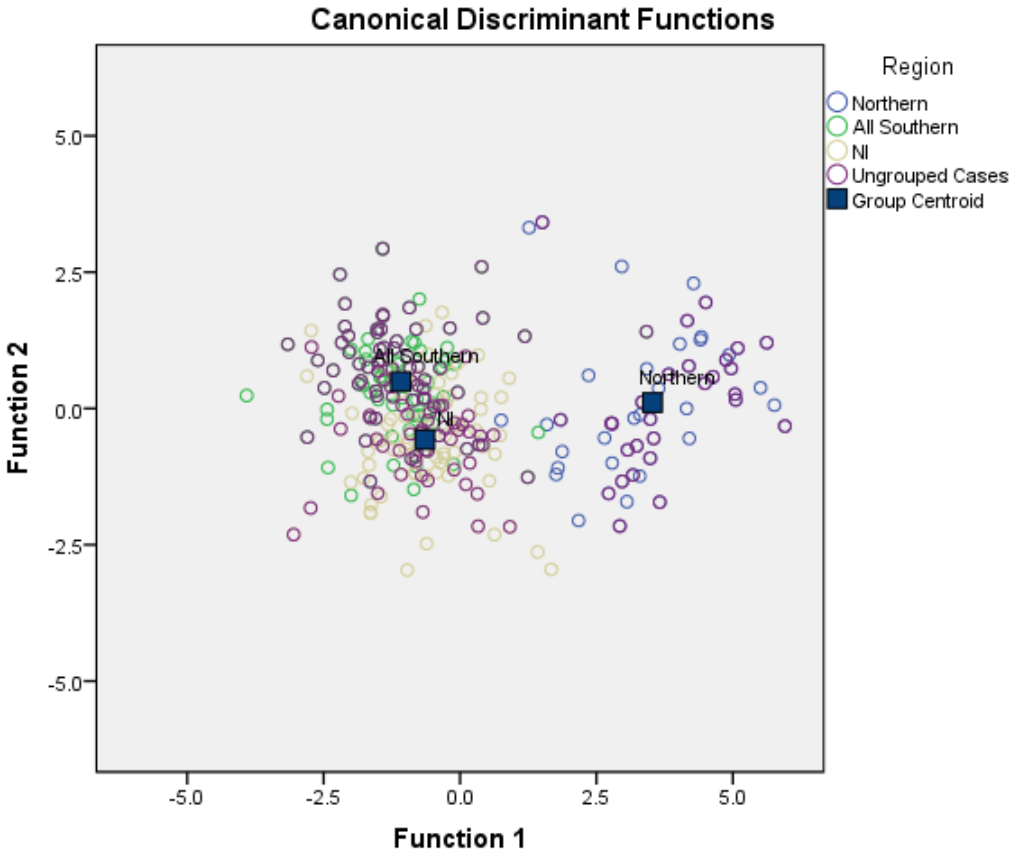


Figure 8.22 - Discriminant function plot of three sampling regions and random samples ('ungrouped cases')

The randomly selected samples are plotted against the geographic groups (figure 8.22), the classification results (table 8.23) indicate that the majority of the 137 random samples are assigned to the Southern + Transitional group (59, 43.1%).

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Northern	S + T	NI	
Original	Count	Northern	52	1	1	54
		S + T	1	81	30	112
		NI	0	24	83	107
		Ungrouped cases	29	59	49	137
	%	Northern	96.3	1.9	1.9	100.0
		S + T	.9	72.3	26.8	100.0
		NI	.0	22.4	77.6	100.0
		Ungrouped cases	21.2	43.1	35.8	100.0
a. 79.1% of original grouped cases correctly classified.						

Table 8.23 - SPSS classification results: predicted membership of 137 blind samples

Overall, the randomly chosen samples were correctly assigned 82.4% of the time (table 8.24).

Group	Number of samples	Correctly classified %	Incorrectly classified %
Northern	28	100	0
S + T	67	76.1	23.9
NI	42	85.7	14.3
Total	137	82.4	17.6

Table 8.24 – Classification of 137 random samples

The results in table 8.24 corroborate those outlined in table 8.1 – the samples from the Northern group have a much higher classification accuracy than those from the other two groups. The Southern + Transitional group has the lowest classification accuracy (table 8.1, 8.24).

A small number of randomly chosen samples were incorrectly classified (24, 17.6%). These samples were from the Southern + Transitional and NI groups. One sample from the Southern + Transitional group was misclassified to the Northern group, but no Northern group samples were themselves misclassified. Sixteen samples from the Southern + Transitional group were misclassified; as mentioned, one to the Northern group, and 15 to the Northern Ireland group. Eight samples from the Northern Ireland group were misclassified, all eight of these were classified to the Southern + Transitional group.

These results are in keeping with those outlined in table 8.1, where samples from the Southern + Transitional and Northern Ireland groups are frequently misclassified to each other. The samples from the Northern group are very rarely misclassified, what is more common is that samples from Northern Ireland and Southern + Transitional are misclassified to the Northern group.

The samples from the Northern group were correctly classified 100% of the time. Within the Northern group, there are three areas: Yorkshire Wolds, Lincolnshire Wolds, and Yorkshire chalk. There were five samples from the Yorkshire Wolds, nine from the Lincolnshire Wolds, and 14 from the Yorkshire chalk.

Classification Results[a]						
		Region	Predicted Group Membership			Total
			Yorks. Wolds	Lincs. Wolds	Yorks. Chalk	
Original	Count	Yorks. Wolds	7	1	0	8
		Lincs. Wolds	1	16	0	17
		Yorks. Chalk	0	0	29	29
		Ungrouped cases	4	10	14	28
	%	Yorks. Wolds	87.5	12.5	.0	100.0
		Lincs. Wolds	5.9	94.1	.0	100.0
		Yorks. Chalk	.0	.0	100.0	100.0
		Ungrouped cases	14.3	35.7	50.0	100.0
a. 96.3% of original grouped cases correctly classified.						

Table 8.25 – Classification of Northern group blind provenancing samples

The blind samples from the Lincolnshire Wolds and Yorkshire Chalk were correctly classified 100% of the time (table 8.25). There was only one misclassified blind sample; a sample from the Yorkshire Wolds was misclassified as belonging to the Lincolnshire Wolds group. The classification accuracy for the Northern province as a whole is 96.3% (table 8.25), whereas the classification accuracy for the blind, randomly selected samples is 96.4% (27/28).

There were 67 randomly chosen samples from the Southern + Transitional group. The classification accuracy for the Southern + Transitional group overall is 67.9% (table 8.26).

Classification Results[a]							
		Region	Predicted Group Membership				Total
			Trans. Prov.	N/S Downs	S Plain/Pewsey	SW Chalk	
Original	Count	Trans. Province	16	1	0	0	17
		N/S Downs	8	34	7	9	58
		S. Plain/Pewsey	2	1	14	3	20
		SW Chalk	1	3	1	12	17
		Ungrouped cases	15	24	13	15	67
	%	Trans. Prov.	94.1	5.9	.0	.0	100.0
		N/S Downs	13.8	58.6	12.1	15.5	100.0
		S. Plain/Pewsey	10.0	5.0	70.0	15.0	100.0
		SW Chalk	5.9	17.6	5.9	70.6	100.0
		Ungrouped cases	22.4	35.8	19.4	22.4	100.0
a. 67.9% of original grouped cases correctly classified.							

Table 8.26 – Classification of Southern + Transitional group blind provenancing samples

Of the 67 random samples, 10 were from the Transitional province, 34 from the North/South Downs, 14 from Salisbury Plain/Pewsey, and 9 from the Southwestern Chalk. The classification accuracy for these samples varied widely: Transitional Province 90% (9/10); North/South Downs 58.8% (20/34); Salisbury Plain/Pewsey 78.5% (11/14); and Southwestern Chalk 77.7% (7/9). The overall classification accuracy for the random samples was 70.1% (47/67).

There were 42 randomly selected samples from the Northern Ireland group, 8 from an inland sampling location and 34 from coastal sites. There was a degree of overlap between the Northern Ireland and Southern + Transitional groups, although 85.7% of samples were

correctly classified to either the coastal or inland sampling locations in Northern Ireland (table 8.24).

Classification Results[a]					
		Region	Predicted Group Membership		Total
			Inland	Coastal	
Original	Count	Inland	16	1	17
		Coastal	19	71	90
		Ungrouped cases	16	26	42
	%	Inland	94.1	5.9	100.0
		Coastal	21.1	78.9	100.0
		Ungrouped cases	38.1	61.9	100.0
a. 81.3% of original grouped cases correctly classified.					

Table 8.27 – Classification of Northern Ireland group blind provenancing samples

The classification results (table 8.27) indicate that some of the coastal samples were classified as inland. One inland sample was misclassified as coastal; nine coastal samples were misclassified as inland. Overall, 32/42 of blind samples were correctly classified to either inland or coastal, a classification accuracy of 76.1%. This is lower than the accuracy for the Northern Ireland group when all pXRF readings are taken into account (table 8.27), however this may be a reflection of the smaller number of random samples.

8.2.7 Blind provenancing tests using ICP-MS

Within this study, a smaller number of samples were subject using acid digestion ICP-MS due to the time-consuming nature of the analysis. Overall, 126 samples from throughout the study

area were examined using this method. To assess the provenancing ability of ICP-MS, samples were selected using the procedure outlined in chapter 5.5.2.

The overall classification accuracy of the pXRF blind provenancing was 79.1% using a three-group separation (Northern, Northern Ireland, and Southern + Transitional) (table 8.1). The ICP-MS results were assessed using discriminant function analysis to determine the optimum numbers of groups. A 9 group separation (coastal NI, inland NI, Yorkshire Wolds, Lincolnshire Wolds, North Downs, South Downs, Transitional, Southwestern Chalk, and Salisbury Plain/Pewsey) achieved a classification accuracy of 60.3%, higher than the pXRF accuracy for 9 groups (51.6%). With the ICP-MS results it was possible to have the samples from Northern Ireland separated into coastal and inland regions. The highest classification accuracy (80.8%) was obtained using a 4-group separation: 1. coastal NI, 2. inland NI, 3. Northern, and 4. Southern + Transitional.

Individually, the classification accuracies for each group are in excess of 70% (table 8.24); the coastal NI group has the lowest classification accuracy at 70.9%, and is misclassified with the Southern + Transitional group 23.6% of the time. The Southern + Transitional group is misclassified as coastal NI 12.1% of the time. The Northern group has the highest classification accuracy at 96.2%.

Classification Results[a]							
		region	Predicted Group Membership				Total
			Coastal NI	Inland NI	Northern	Southern + Trans	
Original	Count	Coastal NI	39	1	2	13	55
		Inland NI	0	9	2	0	11
		Northern	0	0	25	1	26
		Southern + Trans	4	0	1	28	33
		Ungrouped cases	23	5	14	21	63
	%	Coastal NI	70.9	1.8	3.6	23.6	100.0
		Inland NI	.0	81.8	18.2	.0	100.0
		Northern	.0	.0	96.2	3.8	100.0
		Southern + Trans	12.1	.0	3.0	84.8	100.0
		Ungrouped cases	36.5	7.9	22.2	33.3	100.0
a. 80.8% of original grouped cases correctly classified.							

Table 8.28 - SPSS classification results: predicted membership of 63 blind samples

When plotted, the ICP-MS blind provenance samples are widely dispersed amongst the four sampling regions (figure 8.23).

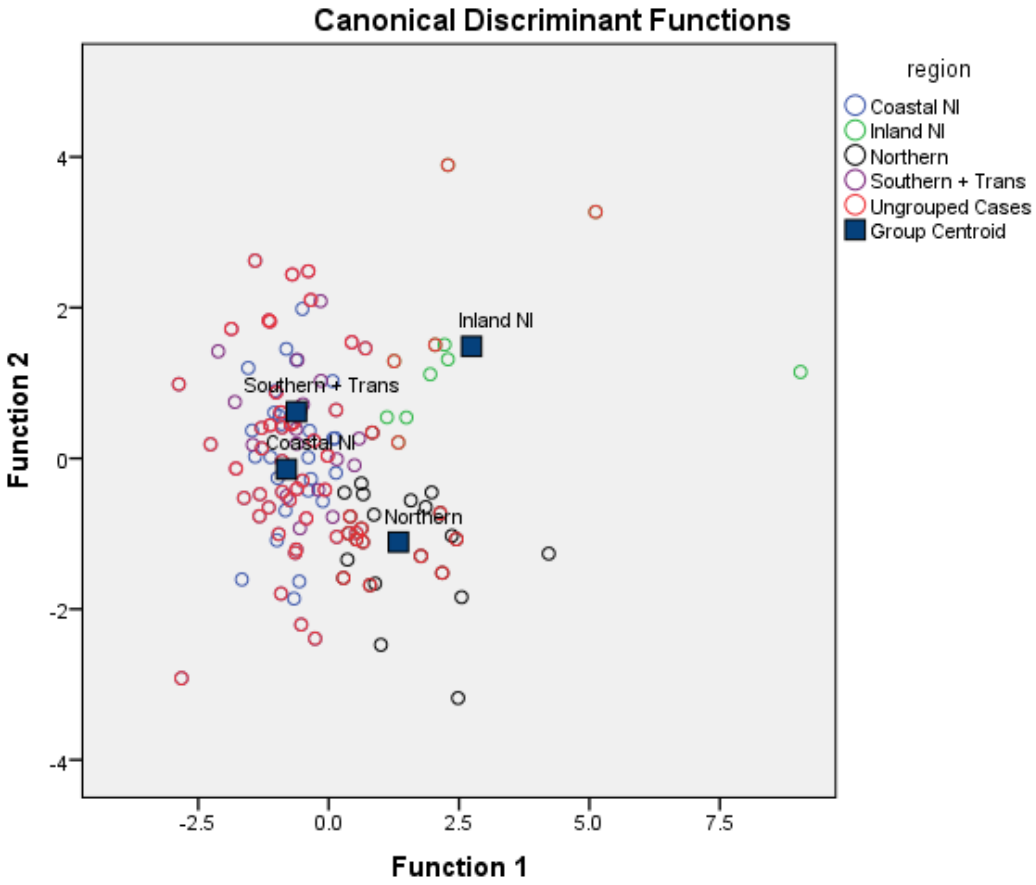


Figure 8.23 – Discriminant function plot of four sampling locations and 63 blind provenancing samples ('ungrouped cases')

The majority of the blind provenance samples are classified to the coastal NI group (23=36.5%), the fewest to the inland NI group (5=7.9%). The predicted and actual group membership of each of the samples is outlined below (table 8.29).

#	Predicted Group	Actual Group	#	Predicted Group	Actual Group	#	Predicted Group	Actual Group
1	Coastal	Coastal	22	Coastal	Coastal	43	Northern	Northern
2	Coastal	Coastal	23	Coastal	Coastal	44	Northern	Northern
3	Coastal	Coastal	24	Inland	Coastal	45	Northern	Northern
4	Coastal	Coastal	25	Northern	Coastal	46	Northern	Northern
5	Coastal	Coastal	26	Coastal	Coastal	47	S + T	S + T
6	Coastal	Coastal	27	S + T	Coastal	48	S + T	S + T
7	Coastal	Coastal	28	S + T	Coastal	49	S + T	S + T
8	S + T	Coastal	29	Coastal	Coastal	50	Coastal	S + T
9	Coastal	Coastal	30	Inland	Inland	51	S + T	S + T
10	Coastal	Coastal	31	Northern	Inland	52	S + T	S + T
11	Coastal	Coastal	32	Inland	Inland	53	S + T	S + T
12	Coastal	Coastal	33	Inland	Inland	54	S + T	S + T
13	Coastal	Coastal	34	Inland	Inland	55	S + T	S + T
14	S + T	Coastal	35	Northern	Northern	56	S + T	S + T
15	Coastal	Coastal	36	S + T	Northern	57	S + T	S + T
16	Coastal	Coastal	37	Northern	Northern	58	S + T	S + T
17	Coastal	Coastal	38	Northern	Northern	59	S + T	S + T
18	Coastal	Coastal	39	Northern	Northern	60	Coastal	S + T
19	Coastal	Coastal	40	Northern	Norther	61	S + T	S + T

					n			
20	S + T	Coastal	41	Northern	Northern	62	S + T	S + T
21	Northern	Coastal	42	Northern	Northern	63	S + T	S + T

Table 8.29 - SPSS classification results: predicted membership of 63 blind samples

In total 63 ICP-MS samples were included in the blind provenancing. Of these, 51 were correctly provenanced and 12 were incorrect, giving a classification accuracy of 80.95%, very close to the 80.8% classification accuracy of the 4-group separation provided from the initial discriminant function analysis (table 8.28), although not vastly better than the 79.1% accuracy obtained by the pXRF 3-group separation (table 8.1).

Only one sample from the Northern group was misclassified; it was classified to the Southern + Transitional group which is not unexpected as the Northern samples are only misclassified to the Southern + Transitional group, and only then 3.8% of the time (table 8.28).

The only Southern + Transitional samples that are misclassified are those placed into the coastal NI group (two instances, table 8.29). Correspondingly, five of the eight misclassified coastal NI samples were grouped with the Southern + Transitional samples. The apparent similarity between the flint from the south of England and north of Ireland demonstrated in the pXRF discriminant function analysis appears to be replicated here.

8.3 Summary

The results from the pXRF and ICP-MS analyses presented in this chapter demonstrate that it is possible to distinguish between the major flint-producing areas of chalk geology within Britain and Ireland. For both methods, the flint sampled from the Northern chalk province has the

highest classification accuracy (96.3% for pXRF, 96.2% for ICP-MS), with a degree of confusion between samples from the Southern + Transitional and Northern Ireland samples.

The pXRF results had an overall classification accuracy of 79.1%; the accuracy of the ICP-MS results was slightly higher at 80.8%. Blind testing of subsets of the pXRF and ICP-MS results provided comparable classification accuracies.

Provenancing the artefact assemblages revealed that the raw material was being sourced from a variety of areas. The Kintyre artefacts were predominantly fashioned on flint from the Northern province, however there was a not insignificant contribution (19/51 artefacts) of flint from the Northern Ireland and Southern + Transitional provinces. Similarly, the raw material used for the Threefords assemblage was sourced mainly from the Northern province. The Nether Exe artefacts were predominantly made from Southern + Transitional province flint, although almost half of the artefacts were made from flint from the Northern province (8/20 artefacts). Interestingly, the artefacts in the N1F recollection assemblage were mainly made from Northern province flint – indicating movement of raw material over 200 miles from the source. Perhaps the most interesting results from this provenancing case study were the details of the Bann Valley assemblage, only 5% of which (3/57) was made from flint from the north of Ireland. The majority of the raw material was sourced to the Northern province.

9.0 DISCUSSION

This thesis set out to investigate the suitability of pXRF and acid digestion ICP-MS to provenance flint within Britain and Ireland. In order to do this, there were a number of aims that had to be addressed:

- Determine chemical composition of flint from primary outcrops of flint (Northern/Southern/Transitional/Northern Ireland)
- Assess difference within and between these areas
- Compare ICP-MS and pXRF in achieving these objectives

Consultation of geological literature revealed that while the formation and extent of chalk outcrops is well understood, the diagenesis of flint remains somewhat obscure (Adams 2008, 6). The chalk outcrops in Britain and Ireland both formed during the Late Cretaceous period, however the chalk in the north of Ireland began forming approximately 20 million years after the chalk in the south of England. At the beginning of this project it was not known what degree of chemical variation would exist within and between the various chalk provinces. The chalk formed through accumulation of calcareous remains of micro-organisms at the bottom of warm, shallow seas during the Late Cretaceous; the chalk itself is relatively pure calcium carbonate, however the high porosity of chalk (20-45%) as well as fissures, facilitate the movement of mineral-laden water that can alter the geochemistry (Edmunds *et. al.* 2002, 9). Towards coastal locations, fissures in the chalk can transmit seawater inland (Hiscock & Bense 2014, 248), potentially altering the geochemistry of the chalk and flint through absorption of minerals from the seawater. Taking these factors into account, the flint could vary quite significantly from one area to another within the same chalk outcrop, depending on local hydrogeological variation as well as porosity of the chalk.

9.1 Methodologies

A comparison of pXRF and acid digestion ICP-MS was conducted to determine which method is most suitable for determining the chemical variation of the flint, taking into account the differences in sample preparation, time taken, suitability for archaeological research, and provenancing 'resolution' that could be achieved. The use of pXRF is well-established in archaeological and geological literature and is a particularly attractive approach for examining archaeological artefacts as it is non-destructive and portable.

Analysis of the flint samples from Britain and Ireland was undertaken using pXRF; in total 273 readings were obtained from four main chalk provinces. The pXRF analysis was quick (60 seconds per reading) and required minimal training. This gave results from 20 elements (phosphorus, sulphur, titanium, vanadium, chromium, iron, copper, nickel, zinc, rubidium, yttrium, zirconium, niobium, molybdenum, caesium, lanthanum, cerium, lutetium, thorium, and uranium) which were converted into relative percentages. This facilitated the comparison of discrete areas within different source regions, and comparison of the regions themselves. Samples were also subject to acid digestion ICP-MS. Due to the extremely time-consuming nature of this analysis, a smaller number of results were obtained (126 samples). Each sample of flint was ground into a fine powder (three-four minutes per sample), weighed out and digested in acid (over four hours per run of eight samples), prior to analysis in the ICP-MS (three-four hours per run of samples).

The ICP-MS sample preparation is destructive – making it less attractive for archaeological research – however the detection limits are much lower and a wider range of elements could

be detected. In total, 20 elements were identified and quantified from the ICP-MS analysis (lithium, beryllium, sodium, magnesium, aluminium, potassium, chromium, manganese, iron, cobalt, nickel, copper, zinc, rubidium, strontium, molybdenum, cadmium, caesium, barium, and lead). The elements used for the pXRF and ICP-MS analyses varied, in part reflecting the lower detection limits of ICP-MS, but also elements that could be quantified using the external standard during ICP-MS analysis.

9.2 Results

9.2.1 Patina

A small study was conducted on the effect that patina may have on geochemical provenancing of flint. The results here were unexpected; samples from Harrow Hill, Southwick Hill, Dover Coast, White Park Bay, and White Rocks demonstrated a significant difference in a number of elements between patinated and unpatinated surfaces. The elements that differed in these samples varied in number from three to eight, and there was frequently evidence of depletion in the levels of silicon in patinated surfaces. This was anticipated as flint is subject to weathering in depositional contexts or while embedded in the chalk, however the samples from Southwick Hill and one sample from White Rocks showed no evidence of silica depletion yet had statistically significant differences in the levels of a number of other elements. The samples from West Kennet demonstrated no statistically significant differences between patinated and unpatinated surfaces yet one fragment had evidence of depleted silica. The process of patination is not yet fully understood and these results indicate that the process does not occur uniformly or predictably.

9.2.2 Differentiating between Britain and Ireland

Starting at a broad scale, the pXRF and ICP-MS analyses demonstrated that flint from Ireland and flint from Britain can be distinguished, and that smaller areas within Britain and Ireland can be differentiated, with one exception (table 9.1).

Differentiating between…	*Elements with statistically significant variation*	
	pXRF	**ICP-MS**
Britain and Ireland	Iron, Zinc, Cerium	Magnesium, Aluminium, Molybdenum
Southern and Transitional	None	Nickel, Copper, Molybdenum
Northern and Transitional	Calcium, Titanium, Manganese, Cobalt, Cerium, Praseodymium, Ytterbium	Manganese
Southern and Northern	Manganese, Iron, Cobalt, Cerium	Molybdenum
Within Northern Ireland: Inland and Coastal	Phosphorus, Titanium, Zirconium	Barium, Manganese

Table 9.1 – Differentiating between flint samples from Britain and Ireland using pXRF and ICP-MS

It was not possible to distinguish between flint samples from the Southern and Transitional groups using pXRF, however the ICP-MS analysis could achieve this.

Within the Northern and Southern chalk provinces there are a number of smaller geographic areas that (with some exceptions) could be separated on the basis of flint geochemistry (table 9.2).

Differentiating between…	*Elements with statistically significant variation*	
	pXRF	**ICP-MS**
Within Northern Group: Chalk and Wolds	Phosphorus, Chlorine, Iron, Cobalt, Copper, Cerium	Chalk flint not sampled for ICP-MS
Within Northern Group: Yorkshire Wolds and Lincolnshire Wolds	Chlorine, Potassium, Titanium, Manganese, Cerium, Ytterbium	Iron, Lead
Within Southern Group: South Downs and North Downs	Titanium, Cobalt, Zirconium	None
Within Southern Group: South Downs and Southwestern Chalk	Cobalt, Nickel	None
Within Southern Group: South Downs and Salisbury Plain/Pewsey	None	Copper
Within Southern Group: North Downs and Southwestern Chalk	Titanium, Nickel	None
Within Southern Group: North Downs and Salisbury Plain/Pewsey	Zirconium	Lead
Within Southern Group: Salisbury Plain/Pewsey and Southwestern Chalk	Titanium, Phosphorus	None

Table 9.2 – Differentiating between flint samples within the Northern and Southern chalk provinces using pXRF and ICP-MS

The ICP-MS analysis did not detect significant differences in the levels of any element that successfully distinguish between most of the areas within the Southern group. This may be to

do with the relatively small number of samples collected from these areas, or the homogeneity of the flint itself. The areas within the Northern province could be more successfully separated using pXRF; the chalk flint and the flint from the Yorkshire and Lincolnshire Wolds can be differentiated using multiple elements using pXRF. This was anticipated as the Wolds flint has been exposed to a variety of different weathering processes, and has had the opportunity to absorb minerals from the soil.

The coastal sampling locations in the north of Ireland proved more difficult to distinguish (table 9.3). There were a number of locations that could not be distinguished using either pXRF or ICP-MS, and two pairs of locations that could not be distinguished at all; Garron Point and Cloughastucan, and Portbraddan and White Park Bay. The inability of both pXRF and ICP-MS to distinguish between these pairs of locations is not surprising, as Garron Point and Cloughastucan are geographically very close to each other, as are Portbraddan and White Park Bay, whose flint samples were obtained from a chalk outcrop that is contiguous between both sites. Overall, Cloughastucan appears to be the most difficult to distinguish from other coastal sources. The difficulties encountered with some of the sampling locations within Northern Ireland may be due to the relatively small area within which the samples were collected; the chalk in Northern Ireland may simply be too chemically homogeneous to allow for more specific provenancing. Alternatively, it is possible that increasing the number of samples collected from this area may result in greater provenancing resolution.

Differentiating between…	*Elements with statistically significant variation*	
	pXRF	**ICP-MS**
Ballintoy and Garron Point	Phosphorus, Zirconium	Magnesium, Copper
Ballintoy and White Rocks	Potassium	Strontium, Lead
Ballintoy and White Park Bay	Zirconium	Magnesium
Ballintoy and Portbraddan	None	Strontium
Ballintoy and Cloughastucan	Phosphorus, Zirconium	None
Garron Point and White Park Bay	None	Copper
Garron Point and Portbraddan	None	Cerium
Garron Point and Carnlough	Carnlough not sampled for pXRF	Copper, Beryllium, Chromium, Cerium
Garron Point and White Rocks	Phosphorus, Potassium, Zirconium	None
Garron Point and Cloughastucan	None	None
Carnlough and Ballintoy	Carnlough not sampled for pXRF	Cobalt
Carnlough and Portbraddan	Carnlough not sampled for pXRF	Molybdenum, Cobalt
Carnlough and White Park Bay	Carnlough not sampled for pXRF	Chromium, Iron
Carnlough and White Rocks	Carnlough not sampled for pXRF	None
Carnlough and Cloughastucan	Carnlough not sampled for pXRF	None
White Rocks and Portbraddan	Potassium, Iron	Magnesium
White Rocks and White Park Bay	Phosphorus, Potassium, Titanium, Zirconium	None
White Rocks and	Phosphorus, Potassium,	None

Cloughastucan	Lead, Copper, Zirconium, Praseodymium	
White Park Bay and Cloughastucan	None	Lead
Portbraddan and Cloughastucan	None	Lead, Copper
Portbraddan and White Park Bay	None	None

Table 9.3 – Differentiating between flint samples from coastal locations in Northern Ireland using pXRF and ICP-MS

This study has demonstrated that different areas of flint-bearing chalk within Britain and Ireland can be distinguished on the basis of the chemical composition of flint samples using ICP-MS and pXRF. The results provide corroborative data for published literature regarding geochemical provenancing of flint (Rockman 2003; Hughes *et. al*. 2010; Högberg *et. al.* 2012; Pettitt *et. al*. 2012) which collectively demonstrates proof of principle, that provenancing flint is possible, but with a caveat that some areas are more difficult to provenance within than others.

The results of the pXRF and ICP-MS analyses were largely in keeping with what was anticipated at the beginning of the project; namely that the major geographic regions could be differentiated, but that separating samples from smaller areas may prove more difficult. It was also expected that the acid digestion ICP-MS analysis, with the capability to detect a wider range of elements at lower concentrations, would be able to find geochemical differences between samples from proximate locations. This was largely the case, however, the pXRF analysis surpassed expectations in differentiating between sampling locations both within the

Southern Chalk province and the Northern Ireland chalk group. The ICP-MS analysis was able to distinguish between the Southern and Transitional chalk provinces, whereas the pXRF analysis could not.

It was not possible to distinguish between all of the locations sampled for this study (tables 9.2, 9.3). The areas that were most difficult to separate geochemically are located within the Southern and Northern Ireland chalk provinces. The reasons for this are not well understood as an increase in samples may provide greater clarity, although it may be the case that the chalk in these areas is not sufficiently chemically heterogeneous to allow small-scale provenancing.

9.2.3 Direct comparison of pXRF and acid digestion ICP-MS results

In order to compare the results of both methodologies, two samples – one from Middleton Quarry and another from Rifle Butts) were analysed firstly with pXRF and then subsampled for ICP-MS analysis. Due to the different sensitivities and detection limits of pXRF and ICP-MS (with ICP-MS being more sensitive and having much lower detection limits), direct comparison of the results from these approaches was difficult.

The results from the pXRF analysis are expressed in relative percentages and the ICP-MS results are presented in ppb. The results from Middleton Quarry and Rifle Butts will be compared by looking at the elements that are most and least abundant.

pXRF	Middleton Quarry (relative %)	ICP-MS	Middleton Quarry (ppb)
Fe	5.14%	**Rb**	8.1400
Cu	3.40%	**Cr**	1.1450
Cr	0.64%	**Fe**	0.4360
Co	0.61%	**Mn**	0.0790
Rb	0.40%	**Co**	0.0530
Zn	0.36%	**Cu**	0.0300
Pb	0.11%	**Pb**	0.0270
Mn	0.08%	**Al**	0.0130
Mo	0.01%	**Cs**	0.0100
Al	0.00%	**K**	0.0030
K	0.00%	**Zn**	0.0020
Cs	0.00%	**Mo**	0.0000

Table 9.4 – Comparison of pXRF and ICP-MS results from Middleton Quarry

Table 9.4 illustrates the elements in common between the pXRF and ICP-MS analyses, arranged in order from most to least abundant for each method. As stated above there are significant differences in the sensitivity and detections limits of these methods, however it is interesting to note that two of the three most abundant elements (chromium and iron) are common for both pXRF and ICP-MS.

pXRF	Rifle Butts (relative %)	ICP-MS	Rifle Butts (ppb)
Fe	2.79%	**Rb**	5.3940
Mn	1.70%	**Fe**	1.4270
Zn	0.86%	**Mn**	0.8150
Co	0.85%	**Cu**	0.7520
Pb	0.44%	**Cr**	0.6910
Rb	0.24%	**Cs**	0.1830
Cu	0.13%	**Co**	0.0500
K	0.07%	**Pb**	0.0190
Al	0.00%	**Al**	0.0180
Mo	0.00%	**K**	0.0090
Cs	0.00%	**Zn**	0.0010
Cr	0.00%	**Mo**	0.0010

Table 9.5 – Comparison of pXRF and ICP-MS results from Rifle Butts

Table 9.5 shows the ICP-MS and pXRF results from Rifle Butts. Like the results from Middleton Quarry, two of the three most abundant elements (manganese and iron) from Rifle Butts are common to both methods. Iron was also one of the most abundant elements detected in samples from Middleton Quarry using both pXRF and ICP-MS.

9.3 Comparison of ICP-MS and pXRF

9.3.1 Analysis

Two analytical methodologies were utilised during this study; pXRF and acid digestion ICP-MS. This approach was taken in order to provide a comparison between an approach that is portable and non-destructive (pXRF), and a destructive, laboratory-based method of analysis (ICP-MS). The various advantages of disadvantages of each of these methods have been

outlined previously (chapter 5) and will not be repeated in detail here, however their performance in this study will be evaluated and opinions offered on the suitability of these approaches for archaeological research.

The pXRF analysis was undertaken using a handheld Bruker Tracer III-SD spectrometer. The handheld spectrometer itself required minimal training and was easy to use, providing quick results on a large volume of samples (273 in total). Although time on the pXRF was scheduled around other researchers, large numbers of samples could be analysed on a single day, leaving the processing of data until afterwards. The post-analysis processing of the data gathered was moderately time-consuming, requiring conversion of spectra from S1PXRF into Artax software, before compilation into Microsoft Excel and then calculating the relative percentages of each element recorded from each sample.

The acid digestion ICP-MS procedure was more complex, and vastly more time consuming. The amount of time taken is evidenced in the much lower number of completed ICP-MS samples (126) compared to pXRF (273). Prior to ICP-MS analysis, the flint samples were ground into a fine powder using a mechanical ball mill at the Archaeological Sciences Department, University of Bradford. This added further time onto the analysis as samples had be taken to Bradford from UCLan at a time that was mutually convenient between myself and the archaeology staff there. The ball mill required cleaning with acetone prior to grinding samples, as well as between each sample to reduce the possibility of contamination. This was time consuming as it had to be as thorough as possible, the maximum number of flint samples processed on a single day was c.20-25, resulting in 5-6 days spent on grinding flint samples alone. The sensitivity of the ICP-MS is perhaps its greatest strength, however this greatly increased the

potential for contamination to be detected and necessitated stringent laboratory procedure in the cleaning of the equipment used, and the precision with which samples must be weighed out (0.04g per sample). The acid digestion procedure required the use of a microwave that heated the samples in pressurised vessels. This stage took several hours to digest a maximum of eight samples; at best two lots of eight samples were processed in a day, however frequent failure of certain microwave components (particularly the turntable and the fibre optic temperature sensor) resulted in runs of samples that were not correctly heated, or held at the requisite temperature, and had to be disposed of. Once prepared, however, the samples could be run *en masse* through using the autosampler accompanying the ICP-MS, taking about 3 minutes per sample. Post-analysis processing of data was straightforward as the ICP-MS results can be transferred into Microsoft Excel from PlasmaLab.

Overall, the pXRF analysis was of great benefit to the study as it facilitated the gathering of large amounts of data with minimal sample preparation. The benefits of pXRF to the archaeologist are obvious as the use of a powerful analytical method in the field, coupled with the ease of use and the ability to rapidly gather data, could inform (and transform) excavation procedure and provide targets for greater investment of effort. The ICP-MS analysis was extremely time-consuming, however this was due in part to the time required to transport samples to Bradford for grinding and the unreliability of the microwave used for acid digestion. The sample preparation for pXRF was undemanding, although, as with the ICP-MS constant vigilance was required to prevent contamination. Despite the laborious acid digestion process, ICP-MS remains the 'gold standard' of highly sensitive multi-element analysis (Flanagan *et. al.* 2013, 105), allowing the simultaneous detection of a large range of elements from a very small sample.

9.3.2 Cost

Cost is perhaps one of the most influential factors when choosing an analytical method, in addition to availability and 'turn-around' time for analysis (Price & Burton 2012, 125). An ICP-MS instrument represents a significant initial investment (c.$180,000/c.£124,000, (Wilbur 2005, 2)) with high running costs due to the need for maintenance of components such as the nebuliser, pumps, and gas supply, as well consumption of argon that generates the plasma (quoted as $10,000/c.£6900 annually (Klockenkämper & von Bohlen 2015, 406)). In addition to the capital required for the purchase and maintenance of the ICP-MS, the acid digestion process necessitates the use of a microwave capable of heating samples under pressure, and a ball mill to grind solid samples into powder. This may result in a prohibitive expense, especially when compared to the cost of a pXRF spectrometer (£20-40,000) which has lower running costs (Ramsey 2008, 44) and minimal sample preparation. The pXRF spectrometer is not without its drawbacks, however the speed with which results can be obtained for a comparatively low investment, including the non-destructive nature of the analysis, makes it a very attractive approach.

9.3.3 Artefact provenancing using ICP-MS and pXRF

The ultimate goal of this study is to use the information gathered to provenance archaeological flint artefacts. With this in mind, a comparison of ICP-MS and pXRF in relation to artefact analysis is appropriate. The most substantial advantages of pXRF analysis have already been mentioned, namely the non-destructive nature of analysis and the ability to conduct analysis in the field to gain results almost immediately. The non-destructive nature of the analysis is perhaps the most important consideration for archaeological research, as previous methods of

artefacts (particularly stone axe provenancing) have relied on destructive methods such as thin section petrography (Williams-Thorpe 2008, 183); thin section petrography in particular has been criticised for the damage done to specimens for a "minimal increase in knowledge" (Peacock 1998, 19). Artefacts which are rare, significant, or unusual are unlikely to be willingly subjected to destructive analysis (Price & Burton 2012, 125), however it is exactly these kinds of artefacts that are likely to garner the greatest attention from archaeologists.

Apart from the obvious aesthetic ramifications of destructive methods (figure 9.1), removal of part of an artefact precludes future analyses if care is not taken (or if it is not possible) to preserve archaeologically significant features.

Figure 9.1 – Polished jadeite axe which has been sampled for petrology analysis (British Museum 2016)

There are also ethical considerations when considering destructive analysis; archaeology as a discipline is responsible for the curation and preservation of artefacts discovered during excavation, destroying part of an artefact must be considered worthwhile when compared to the potential gain in knowledge (Price & Burton 2012, 253-4). Destructive analyses have the potential to revolutionise our understanding of otherwise enigmatic periods of our history; the petrographic analysis of stone axes from Britain and Ireland revealed hitherto unknown

movements and use of a wide range of lithologies and shed new light on the significance of particular landscape features and raw material types (Clough & Cummins 1979, 1988; Pétrequin *et. al.* 2008).

Provenancing artefacts with acid digestion ICP-MS, which will require removal of a small sample, is unlikely to appeal to the curators of archaeological material when non-destructive methods are available. As mentioned above, there is a not insignificant difference in cost of ICP-MS and pXRF instrumentation. However, a major benefit of ICP-MS analysis is the sensitivity, with minimum limits of detection at parts per trillion (ppt) (Pollard *et. al*. 2007, 60). The sensitivity of pXRF spectrometers is much lower for low atomic weight elements, even if these occur in high concentrations (Stulik & Kaplan 2013, 82). However, for mineralogical samples (such as flint) where heavy elements are of interest, pXRF has significantly lower detection limits compared to other X-ray emission methods such as particle-induced X-ray emission (PIXE) (Johansson & Campbell 1995, 422). With solid samples, the detection limits of pXRF are >10 parts per million (ppm) (Rahaman 2003, 157).

The data gathered during this study forms a foundation for further provenancing work in the future. Other researchers are not likely to use the specific instruments utilised for this study, and therefore the ability to compare the results outlined here and results gathered in future is an important issue. The pXRF results gathered for this analysis were gathered using a spectrometer that was factory calibrated, the results themselves were not calibrated to an external standard. The results were gathered using the same instrument and under the same instrumental settings, and should therefore be internally reliable, they cannot be compared to results gathered using other pXRF instruments and while they may be replicable if the

methodology is followed, they are not reliable or valid – basic tenets of scientific investigation and crucial for evaluation of the analysis by other researchers (Shackley 2012, 2). There have been numerous difficulties with calibration of pXRF instruments, not least the difficulty in comparing the results obtained using different handheld devices (Shackley 2011, 13). Difficulties are also found in the accuracy and precision that each instrument provides for a certain element, and the susceptibility to drift over time; pXRF was not designed for solely archaeological use, the absolute abundance of each element required for provenancing analyses runs contrary to its more widespread application for detecting presence/absence of elements in mining and environmental studies (Goodale *et. al.* 2012, 882). These issues result in a situation where data gathered on one pXRF device are not comparable with other devices, even under the same conditions and using the same settings, nor are results gathered from the same device across months or years due to drift. This is a fundamental problem and one that must be redressed.

Comprehensively characterising the geochemical variability of the flint from Britain and Ireland will require enormous numbers of sample readings, not likely to be accomplished by one person using one instrument over a short time period. It will be a collaborative effort and comparability of the results gathered will be crucial to build up a dataset of results. To achieve this, a rigorous analytical protocol must be adopted, including vital elements such as calibration to widely-available international standard/standards, in addition to working with pXRF manufacturers to develop standard calibrations to reduce inter-instrument variation (Goodale *et. al.* 2012, 882). In doing so, results gathered by different researchers can be compared and research advanced through collaborative work and through sharing of data (e.g. Skinner, Hughes, and Shackley using each other's data to provenance obsidian, data which has

been calibrated to international standards (Shackley 2012, 2). Calibration to standards and full disclosure of instrumental conditions will allow analysts in different areas, and using different instruments, to collectively create a dataset that can be used to provenance raw material (Stern 1995, 320).

Provenancing archaeological artefacts has the potential to greatly increase our understanding of the processes that led to its creation, such as raw material procurement, trade, and manufacture.

The outline of changing perspectives on trade and exchange within archaeological discourse was outlined in chapter 2. In light of the methodologies and approaches that were championed and criticised in culture-historical, processual, and post-processual literature throughout the twentieth and twenty-first centuries, this thesis can be interpreted as being based soundly within the processualist paradigm. The substance of this research is the empirical data produced through the pXRF and ICP-MS analyses, however there is a departure from processual archaeology with the use of this data to inform our understanding of the ideological and symbolic reasons behind the choice of raw material in the Mesolithic and Neolithic.

The results presented here are, in one sense, a point of reference for future researchers who are investigating procurement of flint in Britain and Ireland and how raw material was transported. However what should be emphasised are the insights gained into prehistoric procurement and movement of material remains (and potentially, people) through the results of the case studies. Of particular interest are the results from the Bann Valley artefacts, where a significant proportion of the raw material was matched most closely to raw material sources in the north of England. If this is indeed the case, we can unfortunately never determine if the

raw material movement was the result of anthropogenic action or through trade and exchange networks. If we consider the former, the implications of this are very interesting as it would mean that the raw material was transported in not insignificant amounts over hundreds of kilometres when multiple sources of flint would have been encountered on the way. This suggests that the flint from the north of England was considered worth the effort, perhaps due to ideological or cultural reasons, or as a link to the landscape. If we accept that the flint from the north of England was traded or exchanged through networks reaching across the Irish Sea to the interior of the north of Ireland, this would again suggest that the flint was imbued with value due to its origin or its relative exoticism for the groups that obtained and exchanged it. Either of these interpretations slates interpretations of hunter-gatherer groups in Britain and Ireland as being parochial or insular, and provides evidence for lines of communication across the Irish Sea at a time when some researchers considered Mesolithic marine travel to be an impossibility.

Aside from the stated aims and objectives of this research, the underlying aspiration of this study was to demonstrate the complexity and capability of prehistoric groups in relation to their choices of raw material. The culture-historical and processual conceptualisation of Mesolithic groups in particular was essentially to neuter them of individuality and expression, and reduce their sociocultural activities to basic survival and subsistence. In this sense this research aimed to embrace the attitudes of post-processualist archaeology and to place the results within their cultural, historical, and social contexts.

Taking this into account, using a destructive yet highly sensitive analytical method may appear justifiable, however the study presented here demonstrates that the results obtained from the ICP-MS and pXRF analyses vary little in provenancing capability. There are a small number of

instances where ICP-MS can successfully distinguish between areas that pXRF cannot, although the specificity required of geochemical provenancing is ultimately dictated by the research questions posed; in some cases it may be adequate to determine if flint originated from Britain or Ireland, or from the Northern chalk province or the Southern, in which case non-destructive pXRF analysis could be utilised. For provenancing studies which require a finer resolution, or the differentiation of areas not possible with pXRF, ICP-MS could provide this. Ultimately the analytical method chosen will be determined not only by the analytical and methodological advantages of an instrument, but as outlined above the pragmatic considerations of cost and availability will have an influence.

9.3.4 Future directions

A potential approach for future analyses is Raman spectroscopy. This method detects Raman scattering, which occurs when a material is illuminated using a laser (incident radiation), the energy of the reflected light is predominantly unchanged, however a minute proportion of it has lost or gained energy through interaction with the vibrations of the molecules within the sample; the differences in wavelength between the incident radiation and reflected radiation are characteristics of the material under investigation (Pollard *et. al.* 2007, 84). Raman spectroscopy has been applied to a wide range of materials, however its relevance to this study is its ability to provide a 'fingerprint' of a material based on specific patterns in the vibrational spectrum of molecules (Edwards & Vandenabeele 2012, 54).

The advantages of Raman for analysis of geological material are comparable with those of pXRF: no chemical or mechanical preparation of the sample is required; Raman is non-destructive and can obtain results in seconds; it is widely available commercially and can be

brought to the sample for analysis *in situ*; and sample size can vary considerably (Raman can analyse both very large (e.g. statues, elephant tusks) and microscopic samples) (Edwards 2004, 159). A hand-held Raman device is also comparable in price to a pXRF spectrometer (Pestle *et. al.* 2015, 119-20).

Raman spectroscopy is not without its disadvantages, however. In order to accurately 'fingerprint' material, the data gathered during Raman analysis is compared to a dataset of samples from known reference materials. This study has made a significant start on the characterisation of flint from Britain and Ireland, but as stated previously there is much more sampling of primary outcrops to be done. Without a comprehensive, representative dataset provenancing of flint using Raman will prove difficult. Raman microscopy is susceptible to interference from naturally occurring fluorescent materials, atomic fluorescence, and fluorescence caused by fluorophores incorporated into the material through handling or burial (particularly relevant for archaeological artefacts), although these effects can be circumvented (Smith & Clark 2004, 1140). Sensitivity of Raman microscopy is dependent on the instrument configuration and material under analysis, although it is generally considered to have detection limits c.1000ppm – feasibility studies should be conducted to assess sensitivity and detection limits (Jestel 2005, 140).

A direction for future research may be to combine the use of pXRF and portable Raman spectroscopy, a common approach in art and archaeology (e.g. Duran *et. al.* 2011; Smith & Clark 2004). Raman and pXRF have been used as a bipartite approach to determine both the elemental composition of a sample (pXRF) as well as structural and molecular information (Raman) (Van de Voorde *et. al.* 2014). In an analysis of glyptics (engraved materials used as stamps to indicate ownership, e.g. on letters) made from various cryptocrystalline minerals,

the pXRF analysis provided details of the elemental composition whereas Raman can analyse the organic and inorganic components of a material (Lauwers *et. al.* 2016). Provenancing flint using organic compounds has been trialled on flint samples from Poland and appears to have potential, however the approach used was destructive (Grafka *et. al.* 2015). The benefit of Raman spectroscopy is that is can identify organic elements as well as chemical compounds, whereas pXRF cannot. Using non-destructive Raman and pXRF analyses to investigate the organic and inorganic components of flint would provide full characterisation and potentially aid in provenancing.

Aside from Raman, a possible methodology for future analyses may be laser ablation ICP-MS (LA-ICP-MS). LA-ICP-MS analyses solid samples by ablating (vaporising) a small area on the surface of an object, around 1,000 x 1,000 microns in area and less than 30 microns deep (Speakman & Neff 2005, 1). The vaporised material is then analysed to determine the concentration of elements present. Laser ablation does involve destroying a small area of the sample, however this is on the microscopic scale and is not necessarily comparable with the destruction involved in petrography or acid digestion ICP-MS. Depending on the circumstances and when compared to other methods available, LA-ICP-MS may be the least damaging option (Jeffries 2004, 313). The advantages of LA-ICP-MS in comparison to other surface analysis methods are ease of calibration, speed of analysis, and relatively low detection limits (Becker 2007, 283). As mentioned above, LA-ICP-MS is a surface analytical method, a considerable disadvantage if the sample is not chemically homogeneous. LA-ICP-MS is also not as sensitive as acid digestion ICP-MS, with detection limits in parts per million for some elements (Lankton *et. al.* 2008, 339). LA-ICP-MS is also subject to polyatomic interferences when the plasma does not break the sample into monoatomic ions, a particularly significant effect with high

abundance ions, leading to inaccurate results (Zakrzewski *et. al.* 2016, 348). The sample size for LA-ICP-MS is constrained by the dimensions of the analysis chamber, which may require larger objects to be cut or sectioned to allow them to fit in. This is not an issue for geological samples however for analysis of artefacts this may be unacceptable.

The value of LA-ICP-MS has been demonstrated for a wide range of materials, including flint (Pollard & Heron 2008, 55). Provenancing flint using LA-ICP-MS has proved successful (Moroni & Petrelli 2005; Pettitt *et. al.* 2012), however the same considerations apply as for other provenancing methods; large numbers of samples are required to characterise areas of flint-producing geology with good confidence, advantages and disadvantages of each method must be considered, and comparability of the results with those gained from other analyses necessitate careful planning at the analysis stage and processing of data.

9.4 Artefact Provenancing

When separated into three groups, Northern, Southern + Transitional, and Northern Ireland, the classification accuracy obtained using discriminant function analysis is 79.1%. Splitting these regions into more discrete geographic areas reduced the classification accuracy. This indicates that pXRF may be most appropriate for 'broad-brush' provenancing of flint. The samples from the Northern Chalk province are classified with the highest accuracy (96.3%), whereas the samples from the Southern + Transitional group are classified with the lowest accuracy (72.3%). A further complication to provenancing is the frequent misclassification of samples from the Southern + Transitional and Northern Ireland groups, which are incorrectly classified 26.8% of the time.

The Northern Chalk province samples appear to be more geochemically distinct from the Northern Ireland and Southern + Transitional groups. This is perhaps a reflection of the geological similarity of the Northern Chalk province with the chalk in the north of Europe, and of the Northern Ireland, Southern, and Transitional Chalk provinces and the chalk formations in the Paris Basin and southern Europe.

The Bann Valley assemblage was predominantly (43 out of 57 artefacts) grouped to the Northern Chalk province, with only three artefacts matching with the Northern Ireland group. Similarly, the Kintyre (62.7%) and Threefords (75%) assemblages were largely classified to the Northern group. This is not unexpected as the Northern Chalk province is the closest source of flint to these sites.

The Nether Exe and N1F recollections assemblages were collected from sites in the southwest of England. A much lower proportion of these assemblages were classified to the Northern group, 45% of the Nether Exe assemblage is classified as belonging to the Southern + Transitional group, and over a quarter (26%) of the N1F recollection assemblage provenance to the Southern + Transitional group. Again, this is expected if the raw material was procured locally, although this cannot be verified.

9.4.1 Blind provenancing

The blind provenancing tests were conducted to gauge how reliable the artefact provenancing may have been. The highest classification accuracy of pXRF results (79.1%) was achieved using a three group separation: Northern, Northern Ireland, and Southern + Transitional. The classification accuracy of the blind provenancing was 82.4%.

Within the randomly selected samples, the Northern group was correctly classified 100% of the time, although some samples were misclassified to this group. There was some misclassification between the Southern + Transitional and Northern Ireland groups. This was anticipated as the chalk in the north of Ireland and south of England are stratigraphic equivalents, and are more similar to each other than they are to the chalk in the north of England. As the Northern chalk is geologically more similar to the formations in the north of Europe, it appears that the flint from the north of England is easier to separate from the flint in the Southern + Transitional, and Northern Ireland chalk formations.

Within the Northern group, the samples from chalk flint and the Lincolnshire Wolds are correctly classified 100% of the time; samples from the Yorkshire Wolds are classified correctly 80% of the time, one sample out of five was classified to the Lincolnshire Wolds. The Southern + Transitional group contains a number of smaller regions (Transitional, North/South Downs, Salisbury Plain/Pewsey, and Southwestern chalk); samples from these areas are frequently misclassified, the North/South Downs has the lowest classification accuracy (58.8%). The blind samples from the Northern Ireland group were classified correctly 76.1% of the time, although the inland samples were classified correctly more frequently (7/8, 87.5%), coastal samples were often misclassified – 9/34 were classified as coming from the inland sampling location.

The overall classification accuracy achieved from the ICP-MS results was 80.8% using a four group separation (Northern, Southern + Transitional, inland NI, coastal NI) (table 8.28). The blind provenancing samples were correctly classified 80.95% of the time. The Northern province samples had the highest classification accuracy (91.6%), the samples from coastal NI had the lowest (72.4%).

9.4.2 Results

The results from the ICP-MS blind provenancing corroborate the pXRF findings in that the Southern + Transitional and Northern Ireland groups are frequently confused, particularly the samples from coastal NI. The higher overall classification accuracy with the four-group separation is more appealing and achieves greater provenancing resolution than the pXRF three-group separation; however ICP-MS is a wholly destructive technique and may not justify a marginally better accuracy. With regards the blind provenancing tests outlined here the actual source of the flint is known as the samples were all collected from various sites as part of this research. When analysing an archaeological assemblage, the raw material source can be assigned using the methodology outlined in chapter 5, ultimately however there is no way of being certain. The dataset obtained during the course of this research is not an exhaustive, representative sample of flint geochemistry throughout the entirety of Britain and Ireland, and raw material sources used in the past may have been lost.

The blind sampling outlined in chapter 8 uses large numbers of blind samples to obtain the classification results using discriminant function analysis. The larger the number of samples used in the discriminant function analysis compared to the variables, the greater confidence one can have with the results (Stevens 2009, 248), which some authors arguing that the ratio of samples to variables be in the order of between 10:1 and 20:1 (Brown & Wicker 2000, 214). The current study used readings of 20 elements from 273 pXRF and 20 elements from 126 ICP-MS samples. Taking this study forward, greater numbers of flint samples from the various

chalk provinces could prove beneficial in providing a stronger statistical foundation for the classification of artefacts, and may also provide a means of discriminating between areas that, with the current number of samples, is not possible. Archaeological assemblages of stone tools can number into the hundreds of thousands (e.g. Stainton West excavation discovered c. 314, 000 lithic artefacts the majority of which were made from flint (Oxford Archaeology 2016)). With large numbers of artefacts and large numbers of flint samples, classification using discriminant function analysis would be more statistically sound than when investigating small assemblages (or individual artefacts) compared to a limited dataset of flint samples. This emphasises the need for further sampling throughout Britain and Ireland to build up a comprehensive, representative picture of flint geochemistry.

9.4.3 Secondary sources

Secondary sources of flint are deposits of weathered and eroded material that can be found some distance from their parent rock (Cowell & Bowman 1985, 36); secondary deposits of flint are a mass of intermingled nodules from a huge variety of potential original sources, some of which may now be inaccessible due to sea level rise. The turbulent geological history of Britain and Ireland has seen chalk and flint eroded and transported by ice, post-glacial fluviation, and Tertiary denudation (Briggs 1986, 186). The transformative ability of glacial ice is attested to by the spread of glacial erratics; Irish Sea Till along the south coast of Ireland contains material deposited by southward-moving glaciers, including flint from Cretaceous outcrops in the north of Ireland and microgranite from Ailsa-Craig, an island c.10 miles from the coast of South Ayrshire (Ó Cofaigh & Evans 2001, 435). Considering the extent of outcrops of Cretaceous chalk accessible today, if one adds in the extent of submarine outcrops in the North Sea (Oakman & Partington 2009, 294), the lesser-known outcrops (both terrestrial and submarine) in the south of Ireland (Briggs 2001, 42), and the continental chalk, there are a huge number of

potential original sources of the flint nodules found in secondary deposits. The admixture of flint nodules from a variety of sources makes chemical characterisation of secondary deposits impossible as each nodule will retain the chemical composition of its source.

These factors make the analysis of secondary sources incredibly difficult from a provenancing standpoint. Analysis of artefacts made from secondary sources of flint will lead to misclassification. For example: flint eroded from the Cretaceous chalk in Antrim during the last glaciation that was redeposited in the south of Ireland and then used to make tools will have a chemical signature indicating that it originated from the north of Ireland – this may be explained archaeologically by positing long distance trade networks and movement of raw material, when in fact the flint was locally sourced.

Secondary sources of flint were important sources of raw material throughout prehistory; during the Mesolithic in the Vale of Pickering beach pebbles were used preferentially over chalk flint (Conneller 2007, 233), when obtaining the beach pebbles would have brought people near to the chalk outcrops. Flint tools made from beach flint have been found far inland throughout Britain and Ireland (Stewart 2012, 124). It has been generally held that secondary sources of flint are less appealing for tool manufacture due to the (assumed) inherent weaknesses and fractures caused by weathering and erosion (Butler 2005, 19; Conneller & Schadla-Hall 2003, 90; Cramp & Leivers 2010, 10; Holgate 1991, 9). While this may be true for some secondary sources, flint nodules found in secondary deposits can also be extremely stable; nodules with flaws or weaknesses in secondary deposits are worn down very quickly, leaving behind only the most durable nodules (Briggs 1986, 188). In some cases it is clear even that secondary sources of flint were being used for the production of very finely

crafted tools in areas where chalk flint was abundant, such as at Donegore Hill and Lyles Hills in Antrim (Nelis 2003, 206).

Provenancing artefacts made from secondary sources of flint is no doubt an important issue for raw material studies, however the issues of redeposition as outlined above mean that it will be very difficult. A way of approaching this may be to focus initially on primary deposits (as undertaken in this study) and through comprehensive sampling, creating a dataset that can characterise with good confidence areas where flint is found *in situ*. Moving ahead, this data could aid in determining which outcrops of primary flint have been eroded and contribute to each secondary source. Secondary sources may be partly composed by flint which has weathered out of outcrops that are inaccessible and unable to be sampled, it may therefore not be possible to determine the constituent primary sources of a secondary deposit.

9.4.4 Implications of provenancing study

As mentioned above, provenancing studies have provided great insight into trade networks and raw material procurement in the past. The applications of geochemical provenancing, and the resolution desired, are dictated by the questions asked of the material. For some assemblages it may only be necessary to discover if the flint used was local or non-local, for other assemblages or for rare items more exact sourcing may be required. There are a number of research areas within the prehistory of Britain and Ireland where geochemical provenancing of flint could address issues of trade and movement of raw material. For earlier periods of prehistory such as the Mesolithic, flint scatters are frequently the only evidence that is recovered during archaeological investigation (Anderson-Whymark & Garrow 2015, 69). Interpretation of sites that are predominantly or entirely composed of lithic assemblages relies

on thorough analysis of the artefacts. This includes traditional methods of lithic analysis, focusing on macroscopic features such as flake patterns, retouch, reduction sequences, and identification of raw material (Andrefsky 2005). Regarding flint artefacts, sources of the raw material are posited based on qualities such as texture (Ballin 2002, 7-8), colour (Collins 1983, 6; Donnelly & MacGregor 2005, 55), or appearance of cortex (Berridge & Roberts 1986, 15; Crothers *et. al.* 2000, 39). Raw material provenancing is typically limited to inspection of these macroscopic features as geochemical provenancing can be prohibitively costly for assemblages uncovered during commercial excavations (however see Oxford Archaeology North 2011, 120-1). The attribution of raw material source based on subjective features such as colour is highly problematic, such methods are only effective is the raw material is homogeneous in colour/texture/quality and where it occurs in discrete, localised deposits (Hamdan *et. al.* 2014, 427).

Speculative assignation of the source of raw material for flint artefacts has underpinned narratives of prehistoric trade and procurement, as well as influencing the interpretation of such features as Neolithic monuments, which have been posited as foci for exchange of objects made from non-local material (Bradley & Edmonds 1993, 37). Flint axes made from non-local raw material (non-local raw material identified on macroscopic characteristics outlined above, not geochemical analysis) found on archaeological sites have been used as supporting evidence for discussions of socio-political prominence of certain sites and the existence of hierarchical societies (Smith 2008, 17). Flint axes are, of course, only one strand of evidence, however their use in such debates is based on the assumption that they are being manufactured from non-local flint and traded, which cannot be proven in the absence of geochemical analysis. Analysis of Neolithic stone axes (Clough & Cummins 1979, 1988) has

confirmed the spread of artefacts made from 'special' or 'exotic' material throughout Britain and Ireland through petrological means; a similar study undertaken on flint could reveal the precise nature and geographic spread of the trade in flint axes. This has been attempted on a relatively small scale, the samples acquired from six Neolithic flint mines and analysing eight elements in detail using emission spectroscopy and atomic absorption spectroscopy, demonstrating that it is possible to chemically distinguish between these sites (Sieveking *et. al.* 1972). The current study represents a more comprehensive, yet still preliminary, analysis of the major flint-producing areas of Britain and Ireland. An understanding of the chemical variation of flint throughout the study region is necessary prior to provenancing artefacts. To fully understand the occurrence and frequency of flint tool exchange in prehistory, chemical characterisation of flint sources is of paramount importance (Frachtenberg & Yellin 1992, 149).

10. CONCLUSION

This study has demonstrated that samples of flint collected from primary deposits throughout the major chalk provinces of Britain and Ireland can be geochemically distinguished using ICP-MS and pXRF. The results outlined in chapters 6 and 7 provide proof of concept for provenancing of flint in Britain and Ireland, and represent the first such combination of these methodologies to flint from these islands. Some areas within Britain are more difficult to distinguish, particularly the Transitional and Southern provinces, however this is most likely due to similarities in the geological formation of these areas. The results also indicate that patina can be a barrier to accurate provenancing as the levels of certain elements can vary between the patinated and unpatinated flint. Unexpectedly, these findings are not consistent throughout the study area.

The results gathered from the flint samples collected as part of this study form a dataset to which readings from artefacts can be compared. This comparison allows the provenancing of the artefacts to, at the broadest scale, Northern Ireland, the Northern province, or the Southern + Transitional province. The results of artefact provenancing indicated that the majority of the raw material sources were procured from relatively local sources, with the exception of the Bann Valley artefacts which were manufactured from raw material most likely originating from the north of England.

The methodologies employed in this study, acid digestion ICP-MS and pXRF, are both robust, multielement analyses that have provided broadly comparable results in terms of their ability to distinguish between chalk provinces. The disadvantages and advantages have been outlined already, however perhaps the single biggest advantage of pXRF is the speed at which the user can obtain data in a non-destructive manner, a process for ICP-MS that is prohibitively lengthy when considering the volume of samples that are required to characterise a source area with good confidence. Overall, the ease of use and rapidity of pXRF makes it an ideal instrument for provenancing, despite the ICP-MS providing greater levels of sensitivity with rarer elements. The statistical analyses that are conducted after data gathering are relatively quick when using dedicated software such as SPSS.

The next stage of this research is to vastly expand the numbers of flint samples from primary outcrops throughout the study area. Provenancing raw material requires a comprehensive dataset of all potential source regions. This can only be accomplished by analysing very large numbers of samples. Here, the benefits of pXRF are obvious as rapid throughput of samples can be achieved with ease. ICP-MS sample preparation and analysis is a considerably more time-consuming process. It is difficult to quantify how many samples are required to provide complete characterisation of the geochemical variability of a source region, however when considering the sheer size of the chalk outcrops in the south of England or north of Ireland this figure is likely to be very large. For sources such as obsidian where variation within a source is small, fewer samples are required. Flint is more chemically heterogeneous and will likely require exhaustive sampling. Further sampling may help to tease out differences between the major chalk provinces that were not possible with the samples currently obtained (i.e. between the Southern and Transitional provinces).

When the areas of flint-producing primary chalk outcrops are well characterised, analysis of secondary sources can be undertaken. As secondary sources are simply eroded and weathered primary sources, analysis of secondary deposits of flint could reveal whether they share similarities with known primary sources, and how much of the deposits are composed of flint from primary sources unavailable or inaccessible today.

Moving forward, this research could perhaps benefit from exploration of other multielement analyses such as LA-ICP-MS or Raman spectroscopy. Raman is a non-destructive technique, whereas LA-ICP-MS is quasi-non-destructive – both are capable of detecting a wide range of elements at low concentrations. However neither have the portability and arguably ease of use of pXRF. A combined approach of pXRF and Raman spectroscopy has been utilised for previous provenancing studies, and LA-ICP-MS has been applied successfully to flint sourcing in Britain. Analysis of archaeological artefacts is potentially more difficult with LA-ICP-MS as the dimensions of the sample chamber prohibit insertion of large objects. Raman can be used for *in-situ* analysis and can therefore be applied to large and/or irregular objects.

When the various approaches of pXRF, acid digestion ICP-MS, laser ablation ICP-MS, and Raman spectroscopy are evaluated, it is clear that while individually there may be considerable advantages or disadvantages with each method, the overall the ease of use, portability, speed of sample throughput, and non-destructive nature of pXRF make it arguably the most attractive method. There have been issues raised in wider archaeometrical literature regarding the calibration of pXRF spectrometers and comparability of results obtained using different models. Moving this research forward will require calibration to internationally-available external standard(s) to allow results to be compared to those obtained by other researchers. Provenancing flint within Britain and Ireland is an important step in advancing our understanding of the use of this material, however flint occurs in chalk outcrops throughout

the European mainland and the potential for cross-Channel trade and movement of material within Europe is an exciting avenue for study in the future.

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